Application of filtration and silver-ion based disinfection to purify rainwater for potable uses in rural communities of Mexico

by

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DECLARATION

I, Ilan Adler, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

Signed:

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Date:

This thesis is dedicated to the memory of two very special people,
who in their own way, have made this journey possible:

Ilya Adler,
beloved mentor
and source of inspiration

Carlos Moscoso,
dear colleague and friend,
builder of many RWH systems

ABSTRACT

With growing pressures on water supplies worldwide, rainwater harvesting (RWH) is increasingly seen as a viable option to provide drinking water to an expanding population. However, rooftop runoff is not without quality issues. Microbiological and chemical contamination have been detected in several studies, posing a health risk for consumers. This research explores the use of silver ions, combined with conventional filtration and settling mechanisms, as a safe and affordable treatment method that can be applied at a small scale. The systems were installed and tested in rural communities of San Miguel de Allende, a Mexican semi-arid region, throughout two different periods of fieldwork analyses. Lab-scale models were also implemented at UCL, in order to further refine the technology.

Silver has been known for centuries to be a powerful disinfectant, with no known harmful effects to humans if applied in appropriate doses. However, implementation in small-scale rainwater harvesting systems has received little attention, possibly due to a general perception that it is complicated and/or expensive. The devices studied in this thesis are able to dose silver ions at a relatively low cost, avoiding the use of complex nano-materials. System performance is seen to be highly linked to source water conductivity and ionic strength, highlighting the importance of adapting the technology for the specific case of RWH.

Total coliform elimination efficiencies of up to 99.9% are achieved in the field, with a marked exception where cross-contamination from external seepage occurs. Sites with relatively clean rooftops show an absence of total coliforms in the untreated runoff, compared with others where values as high as 1650 CFU/100 ml are recorded. Disinfection using an emerging technique for bacteriophage detection is investigated in the laboratory, indicating a capacity to inactivate viral particles.

Technology adoption issues are also explored, particularly where increased contamination occurs due to insufficient stakeholder participation. Observations show that the silver ion dispensers themselves require little maintenance, while the other components of the system tend to pose more of a challenge.

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ABBREVIATIONS

AC/DC – Alternating/Direct (electrical) current
CEGE – Civil, Environmental & Geomatic Engineering Dept. (UCL)
CI – Confidence interval
COD – Chemical Oxygen Demand
DI – Deionised Water
DO – Dissolved Oxygen
EE – Environmental Engineering (lab)
EPA – Environment Protection Agency
GAC – Granular Activated Carbon
IC – Ion chromatography
ICP-MS – Inductively coupled plasma, mass spectrophotometry
ICP-OES – Inductively coupled plasma, optical emission spectrophotometry
IRRI-Mexico – International Renewable Resources Institute NA – Not Available
KDF – Kinetic Degradation Fluxion Media
MQ – Milli-Q Water (ultra-pure)
ND – Not detected (i.e. below detection limit of instrument)
RW – Rainwater
RWH – Rainwater Harvesting
SAPASMA – Potable Water and Drainage Authority of San Miguel [from Spanish: *Sistema de Agua Potable y Alcantarillado de San Miguel de Allende*]
SD – Standard Deviation
SEM – Standard Error of the Mean
TDS – Total Dissolved Solids
TNC – Too numerous to count (for microorganisms)
TOC – Total Organic Carbon
TSA – Tryptic Soy Broth
MSA – Modified Scholtens Agar
Voc – Open circuit voltage (voltage measured without any load connected)
Q - Flow

UNITS

Lpm: Litres per minute

rpm: revolutions per minute

ppb: parts per billion (the equivalent to µg/l in water)

ppm: parts per million (equivalent to mg/l in water)

pfu: plaque forming units (used for viral counts)

cfu: colony forming units (used mostly for bacteria)

W: Watts (power)

A: Amps (current)

V: Volts (voltage)

1 INTRODUCTION

1.1 BACKGROUND

Urban and rural communities in developing countries are experiencing increasing difficulties in supplying quality drinking water to its inhabitants (Gleick et al. 2006), a problem exacerbated by climate change and an ever growing demand. In this setting, Mexico is not exempt (Adler 2011). The largely semi-arid northwest area of the country where this study is based on exemplifies the situation: many rural communities lack adequate drinking water, which is usually coming from contaminated wells or overexploited aquifers (Garcia 2006), while others have no access at all to any reliable source, depending on irregular trucks for delivery or on carrying water from distant sources. Few detailed studies have been conducted on the quality of the drinking water, as it varies from one specific community to the other, but the main findings, mostly from Government funded or NGO-sponsored research, include the presence of alarming amounts of fluoride, as well as pathogens and other contaminants (ESF 2006).

In this light, rainwater harvesting (RWH) has been proposed as an alternate drinking water source, particularly for rural areas that are afflicted by water scarcity or deficient quality in their current supplies. A number of countries, such as New Zealand and Australia, have traditionally used rainwater as a main source of potable drinking water. Several regions of India, including the Rajasthan Desert, for example, had a long tradition of storing and consuming rain in buried tanks known as 'tankas' until hand pumps and modern technology were implemented, usually with limited success (Agarwal 1997). The failure to adequately supply India's rural population with drinking water has led many NGOs, such as Akash Ganga in Chennai (2006), to promote the 'revival' of ancient rainwater harvesting technology. The Caribbean islands are another example of heavy reliance on rainwater harvesting for domestic needs. Bermuda, for instance, relied exclusively on rainwater until the 1930s (Fewkes 2006).

Notwithstanding, most RWH projects worldwide, especially in areas where tapped water is widely available, focus on its use as a 'non-potable' source, i.e. not destined for human consumption. The British Standards encourage and promote rainwater collection, but with no mention of its use as a drinking water source (BSI 2009). It defines domestic 'non-potable use' as basically "WC flushing, washing machines and garden watering" (BSI 2009, p. 5). There seems to be a basic mistrust about rainwater in general among policy-makers and Government authorities, possibly because of its association to sewage and drainage in the modern, hydraulic convention of urban planning, or due to the fact that quality control is harder to implement, as compared to centralized systems (WHO 1997; Lloyd & Helmer 1991).

Recent research and an increased worldwide focus on RWH as a substitute for dwindling supplies, has shown that there are numerous quality and health issues

associated with the consumption of untreated, direct roof runoff. So far, the purification and filtration systems built for this purpose are based on older, conventional approaches, with many designs based on improvised and at times, artisanal techniques. There is a noticeable lack of accuracy and scientific research in the realm of RWH, given its relative novelty as a practical field of interest. Yet as in any new and rapidly expanding market, innovation and attention to details are needed, as well as an exploration of potential side-effects, if it is to grow into a model that can be replicated on a massive scale.

1.2 RESEARCH MOTIVATION

In 2007, the Ecology and Environment Department of San Miguel de Allende, a small town located 274 km north of Mexico City, contacted the author through his organization at the time, IRRI-Mexico (www.irrimexico.org), to design and build two pilot rainwater harvesting projects for a community with high fluoride levels in their groundwater. After an assessment of the main candidate sites, a school and a neighbouring rural clinic were chosen for their accessibility (close to a main highway) and enhanced impact on the community members. The project was funded in conjunction with the Ecosystem Sciences Foundation, an NGO with ample experience in watershed management who had also done a comprehensive groundwater quality assessment of the area in previous years (ESF, 2006) and thus had a greater understanding of the health risks associated with high fluoride wells.

RWH was implemented as a means to provide drinking water solely, leaving well water strictly for non-potable uses (i.e. sanitation, washing, etc.). Thus the designs were made accordingly. Storage was constructed using buried cisterns lined with a waterproof liner or geomembrane, with a geotextile underneath for greater protection. The 'lids' were made with beams and concrete, enlisting the help of local community masons and builders. These first projects are reported in ESF (2008).

Despite difficulties and lessons learned, mainly regarding maintenance and shared responsibilities, the systems were successful (most are still in operation). In consequence, the Municipality decided to invest in additional projects, mostly in primary and nursery schools, with the main criteria for selection being (a) fluoride levels in groundwater and (b) water availability (some of the communities didn't have any reliable supply whatsoever). These projects were implemented throughout 2008-2009, funded mainly by the Municipal Government, with partial contributions from the Rotary Club.

It was in this later phase that silver ion devices were added to the systems. The motivation for this was to find an alternative to chlorination as a disinfectant, the side effects of which are amply discussed elsewhere in this report. After an evaluation of the existing options, silver ionisation was chosen due to its durability, ease of maintenance and safety. Contact was made with a Mexican supplier who manufactured the units locally at an affordable cost, making the technology all the more attractive.

Noticing the lack of follow-up and proper scientific assessment on the installed systems on behalf of the local Government and other stakeholders, particularly in terms of efficiency and water quality, I decided to take this on as a full-scale doctoral research project. At around the same time, the opportunity for a scholarship arose from CONACYT (Mexican Council for Science and Technology) and I started my PhD at UCL in September 2009, under the supervision of Dr Luiza Campos and Dr Karen Hudson-Edwards.

1.3 OBJECTIVES

The overall aim of this study is to evaluate and better understand the potential of an alternative, custom designed model for purifying rainwater collected for human consumption. The technology consists of a household filtration system coupled with a device that releases silver ions into the water by applying small electrical currents to a pair of electrodes.

The specific research objectives are:

a) Analyse the performance of actual systems installed in rural communities throughout the municipality of San Miguel de Allende, located on the semi-arid central highlands of Mexico.

b) Assess the effect of water quality parameters on the system's efficiency at a lab scale, comparing and contrasting different water sources, with a particular emphasis on rain.

c) Optimise the potential applicability of silver ions in the field, focusing on small-scale, appropriate technology systems, by comparing different devices and model designs.

d) Understand the mechanism of silver ion generation with electrolysis and their behaviour throughout a typical small-scale RWH system.

e) Evaluate the effect of varying silver concentrations on indicator microorganisms, particularly viral particles (bacteriophages) and *E. coli*.

f) Determine silver concentrations in water and correlate to the effect of operational variables such as ionisation time, voltage, water type, flow, turbidity, etc.

g) Test performance of the ionisation device on different types of water with varying conductivities (i.e. tap water, DI and RW), monitoring efficiency of release of silver ions and correlating to electrical variables such as current.

h) Examine common water quality parameters in detail, in raw rainwater as well as at different stages of the model/treatment system.

1.4 THESIS STRUCTURE

Following this introductory section, which has outlined the main objectives and motivation behind the thesis, Chapter 2 presents a literature review of the main technologies existing in the realm of rainwater purification, including relevant topics such as a description of the site in Mexico, water quality, and sampling methods. This is followed by the methodology section (Chapter 3), which details the principal methods chosen both for fieldwork and for controlled laboratory experiments. Chapters 4 and 5 contain the results obtained for each of these, respectively, along with the relevant data analyses. Chapter 6 presents a general discussion of the research as a whole, including a section on the social aspects of technology implementation and adoption of the rainwater harvesting systems used in the field. Finally, Chapter 7 presents overall conclusions of the research project, outlining contributions to knowledge and recommendations for future work.

2 LITERATURE REVIEW

2.1 PREDOMINANT WATER CONCERNS IN AREA OF STUDY

2.1.1 SAN MIGUEL DE ALLENDE

The Municipality of San Miguel de Allende (State of Guanajuato) is located approximately 274 km northwest from Mexico, the capital city. Spawning an area of 1537 km^2, its population is close to 160,000 inhabitants according to the 2010 census (INEGI 2011), distributed between a main town (*Cabecera Municipal* in Spanish) with roughly 46% of the population, and a number of *Comunidades* (rural communities), which have legal and official representation in the figure of a locally elected 'delegate'. The main town, which goes by the same name of the Municipality, is where the local Government offices reside, as well as being the main commercial and cultural hub of the area. The main economic activities are tourism and agriculture (Garcia y Garcia 2006). Industrial activity is minimal. Visitors are attracted to the colonial architecture, hot springs and old churches. In 2008, San Miguel was named a UNESCO World Heritage Site.

The city also attracts a growing number of retirees from the USA, Canada and Europe, which bring in additional economic inputs. However, any benefits from this to the local population are accrued mainly in the city. Even then, the rising cost of property as a consequence of this foreign influx tends to drive out 'locals' from their traditional homes (Dixon et al. 2006).

In contrast, most of the surrounding communities (not to be confused with suburbs), live in conditions of abject poverty and receive far less services than the main town. Some have only dirt roads as their access, which easily get blocked with mud during the rainy season, compounding the sense of isolation. Sanitation, garbage collection and water supply are dismal, in many cases, and tend to get increasingly worse the farther away the community is from the main town. In fact, San Miguel, echoing a condition that repeats itself throughout the entire region, has one of the highest 'inequality rates' in the country (Székely et al. 2007). The link between water scarcity and poverty is inextricable (Hemson et al. 2008), usually compounded by external factors such as climate change (Stoddart 2009).

Historical data reveals an average precipitation of 400-600 mm/year in the region, with internal variations from one part of the municipality to another (SMN 2010). The rainy season normally starts towards the end of May and terminates in early October, followed by a long dry period. These patterns, however, have been changing dramatically in recent years, with sudden heavy storms occurring in the middle of the dry season, or rains starting later than expected. In February 2010 alone, the period for starting fieldwork, 151 mm of rainfall were recorded in the State of Guanajuato, compared to a 6.5 mm average over the past 50 years, representing roughly a 20-fold precipitation increase (CNA 2010b).

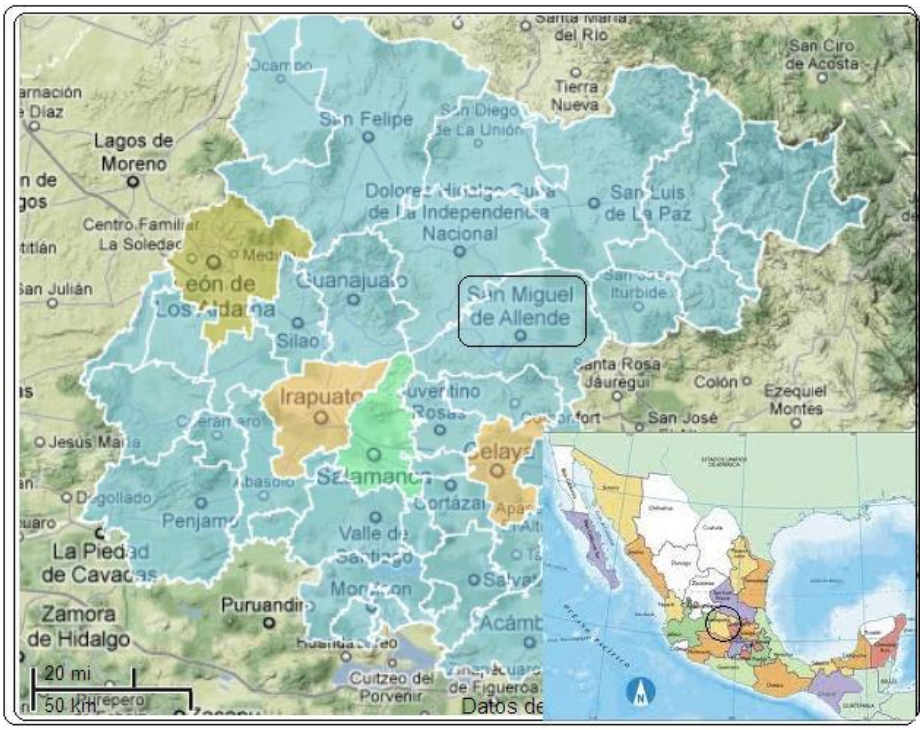

Figure 2.1: Map of Guanajuato State showing location in Mexico (inset) and municipalities. Shades other than blue represent most populated municipalities (INEGI 2011).

2.1.2 CURRENT WATER SUPPLY

At present, there are 810 deep wells[1] operating in the municipality: 15 serving the main town, which relies exclusively on ground water, and 112 supplying drinking water to the rural areas. The remaining wells (over 80%) are dedicated mostly to agriculture (Garcia y Garcia 2006, p.137). The rural communities are rarely connected to the main water grid, since the terrain is hilly in some parts and difficult to access, but rely on local sources, usually independent wells. Streams and natural springs are also used, although in lesser amounts (ESF 2006). In some areas, hot springs are available, which are frequently tapped for recreational purposes, or even for agriculture, after treatment to cool and remove excess minerals.[2]

[1] Average depth is roughly 200m, though there is great variation from one well to another (ESF 2006).

[2] In one of these sites, thermal water is used first for bathing in several pools open to visitors, then passed on to large ponds/ wetlands, and finally used for fish breeding and agriculture.

In most communities, water is pumped to an elevated storage tank, where it is chlorinated (though not always) and gravity fed. To date, there are no installed procedures for fluoride removal or additional filtration. These systems are usually installed and run by the local water authority, SAPASMA, which is publicly owned and the sole authorized water supplier of the region. Appointed community members sometimes aid in maintenance and operation tasks.

In less fortunate cases there will be no water provision whatsoever, and residents will depend on occasional water trucks delivered by the Municipality (known as *pipas* in Spanish), or on hauling water from streams or springs, which are not always closely located to the communities or can be contaminated. In a survey of rural wells, it was observed that over 20% of the sites did not have piped water to their homes (ESF 2006). The latest official census states that over 5,000 homes do not have access to piped or potable water, which represents approximately 15% of the total number of homes in the municipality (INEGI 2011).

Given that this is a semi-arid region, with a rapidly expanding population, akin to the rest of the country, the main aquifer is over-exploited. Wells that supplied large volumes of water only a few years ago are now pumping out a fraction of this amount, with some notorious cases close to the city centre (Garcia y Garcia 2006). Thus rainwater harvesting is not only seen as a quality improvement issue, but also as an alternative source in a region where conventional sources can become very scarce in the near future.

2.1.3 CHEMICAL CONTAMINATION

Budgetary and logistical constraints have so far not allowed continuous and extensive monitoring of rural wells and groundwater sources, which are highly spread out throughout the municipal territory and may be hard to access in the rainy season. Notwithstanding, a general sampling and survey of water supplies is performed at least once a year, with the following general results, which include the effort of independent NGOs:

Arsenic has been evaluated in the area, with no significant finding in any of the wells or surface water supplies surveyed. All samples contained less than 0.05 mg/l, which is the maximum permissible limit according to Mexican drinking water standards (Secretaría de Salud 1994), with the highest recorded level at 0.03 mg/l (ESF 2006).

Manganese has also been reported in some communities, in colorimetric tests performed by the Municipality, particularly in the community of ‘Cruz del Palmar’,

although actual results are as of yet unpublished[3]. Further studies are required for this and other pollutants.

Fluoride in particular is of major concern to local Government authorities, since it can cause a crippling disease known as fluorosis in the long run (Malik et al. 2003). It has been found in concentrations above 4.0 mg/l, highly exceeding the WHO limit of 1.5 mg/l (WHO 2004) in roughly 20% of rural wells surveyed, affecting over 6,000 people (ESF 2006). The presence of this contaminant in groundwater has also been the main motive behind the municipality's decision to implement RWH systems. Thus, a more detailed discussion is presented below.

2.1.3.1 Fluoride and health

The British Geological Survey (2003) summarizes adverse health effects related to long-term exposure in drinking water in the following concentrations:

Dental fluorosis: 1.5 – 4.0 mg/l
Skeletal fluorosis 4.0 – 10 mg/l
Crippling fluorosis: >10 mg/l

It must be noted, however, that actual contraction and symptoms of the disease are also related to other factors, such as general malnutrition, lack of vitamin C or calcium (British Geological Survey 2003). These values also should not be considered as standards or strict guidelines, since numerous other factors affect a recommended maximum intake, for instance, additional presence of Fluoride in air, toothpastes and food (Fawell & Bailey 2006). In fact, the World Health Organization suggests that in some cases "*it would be appropriate to consider setting a standard or local guideline at a [lower] concentration*" (WHO 2004). The current maximum standard for drinking water, adopted by most countries (including Mexico) is of 1.5 mg/l (2004), although this has been challenged by researchers who argue that exposure in lower doses for prolonged periods of time can also have detrimental health effects (Ortiz et al. 1998).

The disease manifests itself as a 'line' or discolouring of the teeth at an early stage (dental), affecting mainly children and the elderly, but eventually reaches the skeletal stage, where it can cause crippling deformities, finally reaching the central nervous system (Burgstahler & Colquhoun 1996). There is much debate as to the true extent of

[3] Source: personal communication with staff from the municipal Environmental Office (DMAE) and from the San Miguel de Allende Water Authority (SAPASMA), during field work in summer 2010.

the effects, whether it is linked to cancer or not, and under what conditions and exposure the disease will actually manifest. Some research points to increasing learning disabilities in children exposed to fluoride in drinking water (Calderon et al. 2000).

Although detailed medical studies have not yet been performed, dental fluorosis is evident in many inhabitants of the affected communities, who tend to have 'lines' or markings of their front teeth, inevitably an early warning sign of potentially more dangerous effects of this disease (Malik et al. 2003).

There is doubt, however, as to the impact of the disease, regardless of the precise extent. Fluorosis has been a cause of economic decline in a large number of communities in Bangladesh and India, where many otherwise healthy adults are no longer fit to work or provide sustenance for their families. An extensive study revealed at least 27 districts with fluoride levels above the 1.5 mg/l standard in semi-arid Rajasthan, the largest state of India (Malik et al. 2003). In the northern city of Durango, Mexico, 97% of the drinking water supplies (including, surprisingly, bottled drinking water) were found to have unacceptably high amounts of Fluoride. The same applies for other regions in Mexico, including the states of Guanajuato (where the present study is conducted) and San Luis Potosi (Diaz-Barriga et al. 1997; Ortiz et al. 1998).

Increases in fluoride, as with other minerals and salts, have also been linked to over-extraction of groundwater from aquifers, which is undoubtedly the case in the San Miguel de Allende area (Ortega-Guerrero et al. 2002; Garcia y Garcia 2006). This is caused by element concentration with decreasing amounts of diluting water. The presence of these elements is also notoriously increased in volcanic areas, where hydro-thermal vents and hot springs can interact with groundwaters used for drinking purposes, depositing sulphur, fluoride and other elements (Dharmagunawardhane & Dissanayake 1993; Diaz-Barriga et al. 1997).

Fluoride is not always easy to remove by economically accessible means, particularly in developing countries.

"In some areas with high natural fluoride levels in drinking water, the guideline value may be difficult to achieve… with the treatment technology available." (WHO 2004)

Although the use of alum and lime are among the most established, commercially used processes, particularly on a large scale (British Geological Survey 2003), in many developing country scenarios these methods may not be easily available. Bone Char, plant carbon and clay filters have been used as low cost alternatives with varying results, with the use of bone and bone char ranking among the most efficient (Phantumvanit & Legeros 1997). GAC has a large number of interferences, and other issues such as large pH changes throughout treatment, as well as a relatively high cost compared to other processes (British Geological Survey 2003).

2.1.4 *MICROBIOLOGICAL CONTAMINATION*

According to the most recently updated official reports, Mexico treats only 35% of its total municipal wastewater production (CNA 2010). With a population of over 100 million, the volumes of untreated effluents with a high microbial load reaching surface waters and eventually contaminating groundwater sources are considerable. Cross-contamination from wastewater discharges, as well as leaky septic tanks, can pose a major hazard to underground aquifers that currently supply potable drinking water (Keyser 1997).

The region of study, San Miguel de Allende, has a wastewater treatment plant, fully functional since 2005, treating the majority of effluents from the main town and some neighbouring suburbs. The treated water is partially reused for irrigation throughout the Municipality, with the rest discharged into a large artificial reservoir named *Presa Allende* (Garcia y Garcia 2006, pp.118-120).

This reservoir is used for irrigation (not for electricity production) with a potential for tourism. However, there is still a considerable volume of contaminated, untreated wastewater that flows into the *Presa*, as well as infiltrate into the soil, where contamination of the aquifer can occur. Furthermore, the more remote communities don't have proper drainage and sanitation services, relying on septic tanks (which are usually not monitored for leaks), and in better cases on independent, smaller 'grids' that will eventually discharge onto a nearby river or stream. In consequence, there is a sizable risk of some wells being contaminated, most likely microbiologically.

Even though the wells of San Miguel have been found to be relatively free from *E. coli*, total coliform counts above the accepted national drinking water standards (Secretaría de Salud 1994) have been found in at least 69 out of over 100 wells analysed (ESF 2006). It is important to bear in mind that total coliforms are used as an indicator group, and the absence of *E. coli* does not preclude the existence of pathogens (Gleeson & Gray 1996). Assessment of other specific microorganisms has not been performed, or was not available at the time of writing.

2.2 RAINWATER QUALITY

Once a rooftop rain collection and storage system has been adequately designed, the issue remains on how to most optimally treat the water for potable uses. The criteria rely on a number of factors, not always easy to resolve: availability of the technology, cost, maintenance involved, rainfall and air quality, expected duration and conditions of storage, etc. Environmental impact and health implications of any disinfection by-products must also be considered.

Rainwater quality studies conducted in different parts of the world have shown an array of potentially pathogenic microorganisms can be present in cisterns or storage tanks, depending on particular atmospheric and roof conditions (Lee et al. 2010). Organic matter from leaves on the roof or debris is also common. Chlorine, for

example, so widely used globally for water disinfection, can react with residual organic matter forming Trihalomethanes and other potentially hazardous substances, posing a serious health risk. Other commonly used techniques for ensuring pathogen removal include: UV treatment, boiling and in certain cases, Solar Disinfection (SODIS). All of these have issues when dealing with drinking water that will be stored for long periods of time, in individual or collectively owned cisterns where regular maintenance is not necessarily guaranteed, as discussed below.

Rainfall has certain quality aspects that make it desirable as a drinking water supply, particularly the low hardness (i.e. low mineral content), which is also beneficial for pipes where clogging and the formation of scale can be a problem (Banks & Heinichen 2006). For this same reason, purification and treatment can be simpler than surface or ground waters with high hardness.

According to the WHO (1997) *"rainwater collected from clean roofs can be of better microbiological quality than water collected from untreated household wells"*. However, issues with rainwater quality have been observed in a number of studies, where minimum compliance with local or international standards is not achieved without filtration or disinfection (Gould, 1999, pp.141-149).

2.2.1 PATHWAYS

The main pathways for contamination in a typical rainwater catching system can be categorized as follows:

Airborne: This refers to contaminants that may be present in the air and collected by the water droplets before reaching the ground. It can include airborne pathogens, exhaust emissions from transport and industry (i.e. sulphuric or nitric acid, causing acid depositions), aerosols, agrochemicals and other substances that are 'sprayed' (Waller et al. 1989). There is also a relationship to the source of the water vapour which ends up as precipitation. Chlorine in rain over oceans, for instance, can reach up concentrations as high as 15mg/l. Similarly, an elevated amount of Ca^{2+} ions has been found in areas where cement industries are present (Appelo & Postma 2005).

Particle deposition is also higher in semi-arid places, such as the study area in Mexico, where wet and dry seasons are clearly marked. This phenomenon is observed at the beginning of the storm seasons, and in long dry spells between rainy events (Egodawatta et al. 2009). In general terms, rainwater quality will also be affected in areas where air quality is poor, due to intense urban or industrial activities, with both chemical and microbiological contaminants (Kim et al. 2005; Kádár & Ragályi 2010).

Catchment surface: Usually the roof or terrain used for collection. This is where most of the pollutants are acquired by the incoming rain (Gould 1999), which can be of a chemical (due to roof composition) or microbiological nature (bird droppings, leaves, debris, etc.). For instance, a study of rainwater quality (Ahammed & Meera 2006) on both cement and galvanised iron roofs shows that while the former presents a considerably greater amount of pathogens, the latter will have a much higher iron, lead and zinc concentration.

Storage: Another important potential source of contamination is the cistern or storage tank(s), where a considerable volume could be held for prolonged periods, if drinking water is to be guaranteed for the dry seasons as well. Microbiological decomposition of organic matter will cause oxygen levels to drop, sponsoring the growth of anaerobic organisms. If minimum light levels are present algae and mould will grow, depending on the type of surface and temperature. Highly resistant biofilms can also form in the bottom sediment or on piping surfaces where bacteria accumulate, given the right conditions (Gleeson & Gray 1996, p.18). In an extensive study, Evans et al. (2009) found an important diversity of bacteria (over 200 species) in rainwater cisterns throughout Australia. Not all of these are pathogenic in nature, however, and in fact a beneficial 'micro-ecology' can be expected to grow in some cases (Evans et al. 2009).

Water quality during storage is also compromised when tanks are not adequately covered, or when sunlight is allowed to seep through, promoting the growth of algae and other micro-organisms. The WHO guidelines on drinking water quality place a strong emphasis on cistern covering for the prevention of mosquito breeding (particularly in areas where there may be malaria or dengue fever), and to avoid the entry of small animals (WHO 1997).

A comprehensive qualitative analysis is furthermore complicated by the individual uses given to rooftops, which vary according to habits, culture and a number of other factors. In Mexico, for instance, roofs are traditionally used to hang laundry, and sometimes to keep animals or pets. In poorer neighbourhoods, even pigs or kitchens for breeding can be found (Rivera et al. 2007). There is also a tendency, given the more lenient weather, for people in the city with lower incomes to live on rooftops (INEGI 2011).

Thus, rainwater collected for consumption in this context could easily contain a rare mixture of laundry detergents, organic animal or human waste, lixiviates from domestic refuse and a host of chemicals from waterproofing paints. This places stringent demands on any treatment method, requiring it to be very 'general' in its effort to eliminate a large number of parameters, or to carefully control the activities, chemicals and debris that accumulates on the catchment area. The latter, however, is not always feasible.

2.2.2 CHEMICAL CONTAMINATION

The compounds affecting water quality that could be potentially observed in any of the pathways described above vary considerably from one rainwater harvesting system to another, depending on local conditions and complex variables such as precipitation, roofing material, temperature and air pollution, among others. A correct evaluation will adjust the parameters to be measured based on the type of surface utilized for catchment.

Yaziz et al. (1989) studied variations in rainwater quality between galvanized iron and tile roofs, showing that despite the former being better in microbiological terms, there was some leaching of zinc when combined with acidic rain. Lead was also found in

high concentrations (up to 254 µg/l) well above the WHO guideline of 50 µg/l, although this was attributed to vehicle emissions from a nearby highway. Since this pollutant has been eliminated from gasoline at a worldwide scale, automobiles are likely no longer a major source. However, more recent studies have found lead to be present in some samples of roof runoffs, albeit in lesser amounts (Lye 2009), since lead is still used in certain paints and roof flashings.

A detailed study in Korea (Lee et al. 2010) comparing the quality of collected rainfall with that of a reservoir shows a high presence of aluminium (over 200 µg/l in selected samples), although other parameters, including lead and zinc, are within WHO standards for safe drinking water. Unfortunately, the study fails to mention what material are the roofs made of, thus not clarifying whether atmospheric deposition or roofing types are the key contributors.

The effect of rainfall intensity is also studied by Yaziz et al. (1989), showing a faster reduction of total solids (more so for metal roofs) with greater intensities, which are measured in the range of 8 – 152 mm/hr, although more research is needed in this regard. The same study concludes that the longer the dry periods between rains, the more pollutants will deposit on roof surfaces.

Where the use of rainwater is widespread, local regulations or practices may encourage the use of specific materials, along with extra maintenance and cleaning procedures. In Bermuda, where rain is used as a key water source, domestic roofs are covered by limestone and sealed with a special latex paint (Fewkes 2006). Extensive chemical analyses by Peters et al. (2008) from over 100 cisterns on the island showed water quality parameters to be within reasonable limits, with the exception of nitrate, found in only 3% of the samples, and lead in 1% of all samples. This study also suggests that dry deposition seems to be a greater source of pollution than roof material *per se*, by analysing sediments in cisterns and comparing them to nearby soil samples, a finding supported by Fewkes (2006). This is however contradicted by other studies, such as Morrow et al. (2010), who show how piping and gutter materials, such as copper or PVC pipes extruded in lead, can contribute significantly to the total chemical element load. The discussion leads to the inevitable conclusion that the concentration of pollutants on RWH systems will display strong site-specific variations.

2.2.2.1 Agrochemicals from atmospheric deposition

In areas of intense agricultural activity, and depending on climatic factors such as prevailing winds, agro-chemicals can make their way into local precipitation. Gould (1999) cites studies in the northeast of the United States where pesticides and herbicides have been found in rainwater. Meera & Ahammed (2006) cite a number of cases in different parts of the world where trace organics such as poly-aromatic hydrocarbons (PAH), organochlorines and organophosphates have been found in roof runoffs, in amounts sufficiently elevated so as to be a cause for concern. A Swiss study (Bucheli et al. 1998) found pesticides in rain and roof runoff, which peaked during and right after application periods. Some average concentrations found were:

Atrazine – 903 ng/l
Alachlor – 191 ng/l
R-Dichlorprop –106 ng/l

2.2.3 BIOLOGICAL CONTAMINATION

Of all three pathways, rooftops and catchment surfaces in general present the greatest probable risk in terms of microbiological quality. Nearby trees will shed leaves, providing substantial organic matter for microbial reproduction. Birds, small mammals such as rodents, and insects, can leave droppings or carry disease-transmitting pathogens. Some roofs, particularly in the dry season, will also tend to accumulate a large amount of dust, which can in turn collect and concentrate airborne pathogens (Banks & Heinichen 2006). Although more research is needed as to the quality of the water, both before and after falling on different types of roof surfaces, some valuable work has been done, part of which is summarized here.

In a comprehensive review of water quality evaluations of rooftop RWH systems worldwide, Meera & Ahammed (2006) show that in the majority of cases, the collected water as it falls directly from the roof does not comply with local or international drinking water standards, such as those proposed by the WHO (2008). This does not mean that rainwater is not a good potential source of drinking water. Particularly in developing countries and rural areas, it can be of much better quality than currently available ground or surface water (WHO 1997, p.99; Gould & Nissen-Petersen 1999, pp.141-149). Just as conventional sources are treated and purified before delivery in most major cities, adequate and affordable purification methods can make rainwater fit to drink, as is discussed in the corresponding section on treatment.

The above review has been complemented and updated by Lye (2009), Signor et al. (2007) and Evans et al. (2007), the latter with a greater focus on the effects of weather patterns and climatic conditions on the deposition of airborne particles, particularly microorganisms. In this regard, another study by the same main author concludes that "weather patterns… can significantly influence the bacterial load of roof run-off" (Evans et al. 2006). This includes wind speed, since it will affect how airborne bacteria and contaminants are transported to rooftops. The frequency and intensity of rainfalls is another contributing factor. Longer periods or dry spells between rains will tend to concentrate a higher number of pollutants, both chemical and biological, in suspended atmospheric particles and on rooftop surfaces (Meera & Ahammed 2006). This however, is influenced by the type and material of the collecting surface. Yaziz et al. (1989), for instance, concludes in a comparative study that metallic roofs which are common in developing countries, such as galvanized iron or zinc, tend to contain less bacterial load than other common roofing materials. This may be in part due to the high temperatures achieved in warmer climates and the lower porosity or particle adherence as compared to, say, concrete.

2.2.3.1 Microbiological issues and health

Although there are enough studies to prove that untreated rainwater is of dubious quality, to say the least, the link between actual health risks and the non-compliance with water standards is more tenuous (Gould 1999). Regulations are usually based on indicator organisms, with many of the standard tests initially designed for wastewater originated from human sources (see Section 2.4.2). This does not necessarily reflect the actual probability of contracting a disease. In a study comparing gastro-intestinal illness on 1000 children consuming solely rainwater against those consuming treated mains potable water, Heyworth (2001) found that occurrence was not greater among the former group. In many rural instances where other sources may be compromised (i.e. arsenic, fluoride), the consumption of rainwater, even untreated, will bring overall health benefits, which have been analysed in detail by some authors (Weeraratna & Ariyananda 2009).

Notwithstanding, there are still potential risks that need to be addressed for rain to become a truly viable drinking water supply. Specific pathogens such as *Salmonella*, *E. coli*, *Campylobacter*, *Legionella*, *Aeromonas*, along with protozoan parasites such as *Giardia* and *Cryptosporidium*, have also been found in rainwater cisterns (Lye 2002; Simmons et al. 2001), and in some studies linked to the incidence of outbreaks, among them: *Campylobacter* enteritis, botulism, diarrhoea and Salmonellosis (Evans et al. 2007). It must be noted, however, that not all *E. coli* are linked to disease, even though there are highly pathogenic strains such as *E. coli* 0157:H7, which can cause Enterohemorrhagic disorders and diarrhoea (Schaechter et al. 1999, pp.190-191).

Maintenance can also be correlated with microbiological water quality, although not much detailed study has been done in this regard. In a 5 year survey done on domestic RWH systems in New Zealand, Abbott et al. (2007) showed that more than half the samples exceeded minimal acceptable standards for *E. coli* and Total Coliforms, but the ones with heavier faecal contamination were precisely those where lack of maintenance, poor design and/or inadequate disinfection, was prominent. More empirical evidence prove this to be the case: water quality can usually be observed to be worse where proper cleaning and maintenance according to manuals or design specifications are not taking place (Adler et al. 2008). Another study in Bangladesh shows that although RWH reduces the health risks from arsenic, which is prevalent in groundwater in several areas, the risk burden for microbial disease is greatly increased. This was analysed using a quantitative health risk assessment model, which takes into account the Disability Adjusted Life Years or 'DALYs' (Karim 2010).

Among all water-borne ailments in the world, diarrhoeal diseases take the leading toll, with over 2 million deaths annually, mostly among children in the lower income sectors of developing countries (WHO 2009; Meera & Ahammed 2006). Interventions to provide safe drinking water and sanitation have been demonstrated to be one of the most powerful tools for prevention. Most interesting and relevant to the present project, Clasen et al. (2007) show how point-of-use interventions, such as RWH and individual household disinfection, can be more cost-effective than conventional source-based interventions, such as centralized distribution and supply. This was

measured in terms of DALYs averted and Cost Effectiveness Analyses (CEA). However, it should be noted that this study emphasizes disinfection interventions (chlorination, etc.) rather than the implementation of RWH per se.

In conclusion, it can be seen that in order for RWH to be truly effective in mitigating diarrhoea and other associated water-borne diseases, the collected rainwater needs to be adequately treated or purified, rather than consumed directly.

2.2.4 CONDUCTIVITY

Conductivity, being an indirect measure of the amount of dissolved ions in the water, can be loosely related to total dissolved solids (TDS) by the following estimate:

TDS (mg/l) ≈ Conductivity (µS/cm) x 0.67

Conductivity will also vary proportionally with temperature. Most modern meters, which consist of a pair of electrodes and a special voltmeter, will have automatic adjustment for temperature. Typical surface water values (i.e. non-contaminated river), will be between 150 – 500 µS/cm (IMTA 2005, p.17).

The analysis of conductivity is relevant for this study, as it will affect the way in which silver ions will be distributed through the water. Presumably, greater conductivity should mean greater efficiency of silver ion disinfection (a hypothesis which, to our knowledge, hasn't yet been fully tested). A brief summary of the main findings for rainwater are presented here.

In general, rain can be expected to have low dissolved mineral content, compared to most surface or groundwaters, and thus low conductivity. Evidently, the collection surface and atmospheric particles will have an effect. Kus et al. (2010) found conductivity values in the initial 0.5mm of rain as high as 307 µS/cm, after contact with a ceramic rooftop, compared to 20 µS/cm from direct rain on the same site (i.e. without touching the roof). However, these readings dropped to less than 100 µS/cm after a first flush of 2 mm, decreasing continuously until reaching values close to those of direct precipitation, suggesting that rainfall is washing out ions from the catchment surface in the first few millimetres of an event.

Jordan et al. (2008) monitored TDS directly in rainwater cisterns in Arizona, with values between 20–150 mg/l (roughly 30-250 µS/cm) in the summer, and considerably lower values in the winter, as expected. The material of cisterns, which in this case were metallic, is of importance. A comparison of a cement/concrete and galvanised iron roof shows a variation in this regard. The cement roof displays slightly lower values (96 compared to 128 µS/cm) (Ahammed & Meera 2006). This is opposite to what Mendez et al. (2010) found in their comparative study of several roof types, where in fact green roofs show the highest conductivity (over 300 µS/cm), while metal and tile display the lowest values. Again, in this case, regardless of roof type all values drop consistently with first and second flushes. Direct precipitation conductivity is also low, ranging from 18-61 µS/cm, which is consistent with an

earlier study performed by Yaziz et al. (1989), where measurements are in a similar range.

Lower conductivity liquids tend to be more corrosive, especially to copper, iron or lead pipes, and will leach metal ions into the water (Duchesne et al. 2013). Some authors even recommend adding small amounts of carbonate or other substances to collected rain or potable water in order to buffer low pH values and increase conductivity (IMTA 2005; Banks & Heinichen 2006).

2.2.5 pH

In general terms, pH in direct rain samples has been found to be acidic, especially where urban or industrial emissions are present, but seems to increase upon contact with roof surfaces (Gould & Nissen-Petersen 1999; Butler & Memon 2006, pp. 49-51). A comparison of cisterns in different locations revealed industrial areas to have higher lead concentrations, while rural areas displayed higher nitrates, possibly due to fertilizers, with a subsequent increase in pH (Thomas & Greene 1993). Acidic water has direct negative consequences for health, given their 'aggressive' tendency to dissolve and leach out heavy metals (and other contaminants) from roofing materials and sediments in the storage tank. Thus, where pH is low, higher lead concentrations in the stored rainwater have been found than what be found under normal pH conditions (Gould 1999). Cistern composition also has an impact. For example, samples taken from common ferro-cement tanks have been found to be more alkaline (Simmons et al. 2001).

The weathering and decomposition of organic matters, as would be expected to occur in a poorly maintained collection surface, will result in a pH drop. This is owing to the additional release of H+ ions that occurs in organic matter degradation (Meera & Ahammed 2006). Wooden roofs are particularly susceptible, especially if they have cracks where rotting leaves, mould and other materials can accumulate. A comparative study of typical roofing materials in Texas, shows wood shingles to be the worst in terms of water quality (Chang et al. 2004). Surprisingly, this also held true for zinc, where concentrations were even higher than in metallic roofs, possibly due to chemical treatments and galvanized components such as nails, etc. which when combined with the more acidic runoff trigger a greater release.

2.3 RAINWATER PURIFICATION

There is a general consensus throughout the literature reviewed that some form of treatment is necessary in order for rooftop collected rainwater to be fit for drinking purposes (Meera & Ahammed 2006). As seen in the previous section, health risks are site-specific and depending on a wide range of parameters, due to the high seasonal and local variability. Thus, it is difficult to suggest a unique 'recipe' or technology that will suit all systems. Availability of materials, local expertise and affordability are also factors that need to be taken into consideration when choosing the most appropriate treatment method, further complicating any decision-making in this regard.

2.3.1 PRE-TREATMENT

2.3.1.1 First flush

Among the systems reviewed so far, the single most powerful and easy to implement tool for rainwater purification is the diversion of the first few millimetres of rain, which are usually the most heavily contaminated (Yaziz et al. 1989; Gould 1999). This has been proven for micro-organisms as well as for many chemical contaminants, even though it is not always easy to quantify. Dennis Lye (2009), from the US Environment Protection Agency, states:

The diversion of this initial 'first-flush'… results in dramatic increase in water quality. However, not enough is known about geographical parameters, the effect of weather patterns, the volumes required, and properties of catchment surfaces to identify exactly what constitutes a 'first-flush'.

In a scientific evaluation of several products and systems to improve rainwater quality, Abbott et al. (2007) determined that first flush diverters caused 'a spectacular reduction in contamination levels', even though the actual volume to be diverted depends not only on the type of roof or local conditions, but also on rainfall intensity and the number of 'dry' days preceding a rainfall event (as mentioned by Yaziz et al. 1989).

Some common 'rules of thumb' (which are not necessarily equivalent) are:

- 20-25 L of a rainfall event
- 2 mm of rain over the roof area
- 5-10 min of a rainfall event
- "Until it runs clear" (cited from WHO 1997)
- First storms of the year

Sources: (WHO 2008; Abbott, Caughley & Ward 2007)

In more recent studies, Martinson & Thomas (2009) show how a properly designed first-flush device can reduce up to 85% of incoming material, using a mass-balance model, while Doyle & Shanahan (2010), conclude from empirical evidence in a Rwandan village that diverting the first millimetre of runoff, after three consecutive dry days, is a good general guideline. They also show an exponential decay of turbidity using this model. A more sophisticated study in Sydney shows that even though common contaminants such as ammonia, TSS, and many heavy metals are greatly reduced in the first 2 mm of runoff (considering an urban area), lead and turbidity are reduced to acceptable limits only after bypassing the first 5-6 mm of rainfall (Kus et al. 2010).

Some designs for first-flush devices, which can also act as sedimentation/ settling tanks, are found in Banks & Heinichen (2006), WHO (1997) and Adler et al. (2008).

2.3.1.2 Sedimentation

Settling is an old technique for clearing water from heavier, sedimentable solids. It was observed in the ancient city of Petra, Jordan, along with a complex infrastructure for capturing and storing rainwater. In one area of the archaeological site, over seven settling tanks in series were found, apparently build by the Nabateans to remove lime deposits before storage in a 'drinking-water basin' (Bellwald & Ruben 2003, pp. 64-65).

The main objective of sedimentation is to 'slow down' incoming rainwater and allow heavier particles to precipitate. A number of products exist in the market to increase formation of flocs, and thus accelerate precipitation, such as aluminium and iron salts. Although these are mostly restricted to potable water treatment plants, some domestic, small-scale applications exist, such as the use of portable 'flocculation-chlorination' packets, which include powdered ferrous sulphate as a flocculant and calcium hypochlorite for disinfection (National Academy of Sciences 2008). Alum and lime have also been used as common flocculants (Vasudevan & Pathak 2000), although the latter acts more as a water softener than a coagulant. The actual overall use of flocculants in household water purification systems, however, is limited (Schmidt & Cairncross 2009).

Most of the recent literature and research in RWH, seems to prefer first-flush systems rather than old-fashioned sedimentation tanks, since these tend to become breeding grounds for bacteria and/or mosquitoes, if not properly taken care of (Banks & Heinichen 2006).

2.3.1.3 Pre-filtering

The main purpose behind these 'pre-tank' systems, as the authoritative "Texas Manual for Rainwater Harvesting" (Krishna 2005) identifies them, is to keep as much organic matter and debris out of the cistern, thus extending the life and efficiency of any post-filtering or treatment taking place. Given the rising popularity of RWH worldwide as an alternate supply source, a number of products for this purpose alone are continuously entering the market, among them: Roof washers, leaf guards, screens and coarse mesh filters, strainer baskets, etc. Many of these simple yet ingenious devices can be found in various RWH manuals and technical publications (Banks & Heinichen 2006; Krishna 2005; Adler et al. 2008).

Grease traps, for instance, such as those used for grey-water treatment, have been adapted successfully to first-flush or sedimentation tanks. This simple action will prevent floating solids or objects from the uppermost incoming layer to flow into the cistern, further improving water quality (Adler et al. 2008).

Abbott et al. (2007) tested a number of these products in New Zealand, including calmed inlet pipes (allowing water to enter near the bottom of the tank without removing sediment), 2-tank systems, to allow for greater sedimentation, vacuum systems that syphon the bottom of tanks, and first flush systems. Their conclusion, based on the removal of indicator microorganisms, was that first-flush diverters alone

were the most effective, although not discarding the improvement in overall water quality from other devices.

2.3.2 FILTRATION

A number of media for filtering water at a household level, also applicable to RWH systems, exist in the market and more are constantly being developed, as demand for quality drinking water increases worldwide. A selection of the most common methods are explored below.

2.3.2.1 Activated Carbon/ KDF

Carbon obtained from charcoal or a number of vegetable sources (such as coconut shell), can be *activated* at high temperatures, in a complex anaerobic process, to create highly porous particles where, notably, a gram will have a surface area of over 500 m^2 (Bitton 1994, p.271). This large surface area is highly adsorbent and will retain a host of contaminants, including chlorine, as well as dissolved organic matter (National Academy of Sciences 2008). The medium needs to be replaced when saturated with contaminants or particulate matter, although its life-span can be increased by adding KDF (Kinetic Degradation Fluxion Media), a zinc-copper alloy with ionic and adsorbent capacities. KDF will also remove chlorine, pesticides and some heavy metals, as well as having bacteriostatic properties (i.e. does not support the growth of bacteria).

Commercial activated carbon filters will tend to form a biofilm when microbiologically contaminated waters flow through them. Although these bacteria can be beneficial for degrading assimilable organic carbon, opportunistic pathogens can also use the biofilm as a protection against disinfection (Gleeson & Gray 1996, pp.19-21). The addition of silver nitrate and KDF to the carbon media is commonly used to help retard this growth.

Point of Use (POU) filters have been tested for RWH use by Jordan et al. (2008), among others. The systems include polyspun cartridges, which basically retain sediments and larger particles (typically over 5 microns in diameter), in order to further protect the activated carbon filter. Their findings show that despite reducing total coliforms, heterotrophic plate counts actually *increased* after passage through the filters. TOC also increased, which suggests that the granular carbon or the trapped sediment in the cartridges are retaining organic matter, possibly acting as a nutrient medium for bacterial growth (presumably non-pathogenic). KDF-55, a more recent variety of commercial KDF, has been effectively tested in a RWH system, displaying powerful disinfection properties (Vasudevan & Pathak 2000).

Activated carbon is applied in powdered, granular (GAC), or extruded form (‘carbon block’). Both GAC and carbon block cartridges, such as the Matrikx-CR1 (see KX Technologies 2010) can be effective in removing protozoan cysts and some bacteria (Bitton 1994, pp.271-274).

2.3.2.2 Sand filters

Both rapid and slow sand filtration have been in use for drinking water purification for a long time. The latter consists of allowing a biofilm to form on the top layer and also within the sand which has found to be effective, if properly maintained, in the removal turbidity and pathogens such as *Giardia*, *Salmonella* and viruses (Bitton 1994, pp.267-270). Rapid sand filtration, less effective but useful for high volumes, relies on precisely the opposite (i.e. no biofilm formation), and thus requires frequent backwashing. In this case, the sand contains components such as gravel or anthracite which will effectively filter at faster flow rates (ibid).

Biosand filters are a small-scale form of slow sand filtration promoted in developing countries as an inexpensive tool for household and community water purification (CAWST 2011). Their efficiency in the removal of bacteria and protozoa has been tested, although further disinfection is usually required for the water to be potable. A recent review suggested that, due to their affordability and ease of maintenance, only ceramic filters and biosand filtration have the potential for sustained uptake and use in lower-income communities (Sobsey et al. cited in Schmidt & Cairncross 2009).

Ahammed & Meera (2006) found sand filters, coated with iron hydroxide, to be effective in the removal of some heavy metals (zinc, lead, iron) and bacteria from roof-harvested rainwater. They also determined regular sand filtration to be inefficient in removing bacteria, especially when a biofilm was not allowed to form. The addition of metal hydroxides is relatively simple and can be used to greatly enhance the filtering/adsorption power of these filters. Iron hydroxide has also been found to be effective for the removal of arsenic and other contaminants (Lukasik 1999).

2.3.2.3 Reverse Osmosis (RO)

RO was used as a pilot system in one of our first RWH projects implemented in San Miguel de Allende, in the community clinic of Augustin Gonzalez (ESF 2008). A household 5-stage, 50 Gallons per Day (GPD) unit, was installed inside the clinic, after the standard filtration systems, to further improve water quality for both staff and patients. RO is one of the most sophisticated water purification methods available at a household level. It will effectively remove several compounds that conventional filters can't eliminate, including calcium, magnesium (i.e. reducing hardness), bacteria and even viruses, to a certain extent, though they are usually combined with some form of disinfection method such as UV (Campbell 1983, pp.131-132).

A semi-permeable membrane allows the solute to pass (water), leaving behind most salts and macro-molecules (solutes) on the other side. These membranes can be made of cellulose acetate, nylon or nano-structures made of polyamides, also known as thin film composite membranes (TFC). They can also partially remove hazardous substances which are otherwise hard to eliminate, such as NDMA, a disinfection by-product of chloramine (Mitch et al. 2003).

In the case of rainwater, RO is convenient given the low level of minerals contained in the source water (compared to most conventional sources). Membranes will act smoothly and will rarely require servicing as long as the adequate pre-filtering is taken care of, to remove particles and chemicals that could potentially harm the membrane (Banks & Heinichen 2006). For this reason, most modern units are equipped with a number of pre-treatment stages, involving fine particle and activated carbon filters.

Despite its effectiveness, RO has several well documented drawbacks (Campbell 1983):

- It consumes energy; the membrane needs to be pressurized in order to overcome the natural osmotic pressure. In a conventional household system, pressures between 200-400 psi may be required, depending on the type of source water.
- Only a portion of the incoming fluid is actually filtered, the rest is considered 'reject water'. Typically, for every 3 L of incoming liquid, only one litre of purified water is produced. This drawback was overcome in the clinic system by using the rejected water for toilet flushing and other appliances.
- Systems tend to be complex, with many stages and variables that need to be monitored, including pressure, pump operation, maintenance and replacement of cartridges, etc.
- It is not entirely efficient as a disinfection system, and thus, despite its high cost, compared to conventional POU filters, it still requires additional purification technology. Total bacterial counts of up to 10,000 CFU/ml, including potentially risky species like *Pseudomonas,* have been found in purified effluents (Bitton 1994, p.290).

2.3.3 DISINFECTION

2.3.3.1 Chlorine

It is believed that nearly 80% of the US population is exposed to some form of chlorine, from drinking water purification processes. The same can be said for Mexico and many other countries where chlorination is the primary method of disinfection (Bitton 1994). Chlorine is usually applied to water in the following forms:

- Hypochlorous acid (HOCl) and hypochlorite (OCl-), both formed from hydrolysis of chlorine gas and collectively known as 'free chlorine'
- Chlorine dioxide (ClO_2)
- Mono-chloramines (NH_2Cl)

The main biocidal actions, depending on the method used and the type of microorganism involved, consist of: (a) damaging the cell membrane, and (b) disrupting nucleic acids (RNA, DNA) and enzyme production. The latter appears to be the mechanism for inactivation of virus, although damage to the capsid or protein

coat could be the target in some types viruses (Vaughn and Novotny 1991, cited in Bitton 1994, p.120).

In general terms, protozoan cysts are the most resistant microorganisms to disinfection by chlorine (i.e. *Giardia, Cryptosporidium*, etc.), followed by several strains of virus and finally vegetative bacteria, thus the inadequacy of coliform indicators for completely assessing pathogenic contamination of water (see Section 2.4.2). Of all types of chlorine available, HOCl and ClO_2 are among the most powerful, with chloramines being the less effective (Bitton 1994, pp.118-125). The later, however, are increasingly preferred in water purification systems, due to their ability to control biofilm formation in tanks and distribution systems (Le Chevalier et al.1990, cited by Bitton 1994). Bacteria can also form biofilms in activated carbon filters, displaying increased resistance to chlorination (Bitton 1994, p.273). Chloramination appears to be more effective in controlling these resistant strains than free chlorine or chlorine dioxide.

Disinfection by-products (DBPs) are a major issue when chlorination is applied to water containing organic matter and nitrogen compounds (which can easily be the case in rainwater collected from unclean roofs). Trihalomethanes (chloroform or THMs) and Haloacetic acids will readily form when free chlorine (or bromide) is combined with natural organic matter, such as humic acids produced from decaying plant matter (McDonald et al. 2013). THMs have been linked to cancer, as well as spontaneous abortion, liver, kidney and central nervous problems, and are currently regulated by the USEPA (Xie 2004, p.3).

Chloramines are known to produce less THMs, and are another reason for their popularity despite their lower efficacy, but are now increasingly linked to the formation of a yet more dangerous compound and probable carcinogen: NDMA (N-Nitrosodimethylamine). Its formation is complex and the mechanisms not yet fully understood, yet increasing concentrations are being found in drinking water sources that use chloramines as a disinfectant. This compound is not easily removed by conventional filtration methods; in fact, GAC may promote its formation by surface catalysed reactions, or the presence of a nitrifying biofilm (Mitch et al. 2003).

Total Organic Carbon (TOC) is also correlated to the formation of THMs and other by-products. Adding to the fact that actual disinfection is less efficient in the presence of high turbidity and/or particulate matter, it can be seen that chlorine should ideally be applied to relatively clear or filtered effluents, in order for it to be most effective (Bitton 1994). In the case of small-scale RWH this is not always possible, and adding chlorine tablets directly to cisterns which have not been pre-filtered, may result in a complex chemical chain occurring, involving the formation of chloramines (from excess chlorine reacting with free ammonia or nitrogen compounds), THMs and potentially NDMA.

Iodine behaves much like chlorine and is commonly used as a disinfectant for small-scale, portable applications, with the advantage that it does not react with ammonia to form hazardous DBPs (Campbell 1983, pp.141-142). It is, however, much more

expensive than chlorine and is rarely used for continuous water purification requirements, such as RWH, and is thus not covered here in detail.

2.3.3.2 UV

Ultraviolet light was first used in the early 20th century in the USA. It has been gaining increasing popularity as an rapid, efficient and simple POU disinfection device, as well as in larger water purification plants (Bitton 1994, pp.129-134). UV radiation, at around 260nm wavelength, attacks the DNA of microorganisms and virus. It can also eliminate hard to remove protozoan parasites such as *Giardia* and *Cryptosporidium*, although at higher doses. UV has also been found to be effective in the degradation of some hazardous chemicals by photolysis, notoriously NDMA. However, the dosages required for such removal are up to 10 times higher than what would be required for drinking water disinfection (Mitch et al. 2003).

UV is popular in many small-scale RWH systems worldwide, and is promoted in a number of manuals and practical guides (Krishna 2005; Banks & Heinichen 2006). Jordan et al (2008) tested a typical household POU filtration system combined with a conventional low-dose UV lamp, finding effective removal of indicator bacteria and virus (water was 'spiked' with *E. coli* and MS2 viral bacteriophage). Heterotrophic plate counts were not totally removed (around 98%) suggesting possible microorganism regrowth after treatment.

Among the drawbacks of UV treatment for rural areas in developing countries are:

- Relative high cost of equipment and lamps, which need to be replaced periodically
- Disposal of lamps may pose an environmental hazard issue where recycling is inadequate, since the UV is generated by a mercury vapour lamp
- There is no residual, thus possibility of re-contamination in stored water
- Constant supply of electricity required (lamps highly sensitive to voltage peaks)
- Turbidity or suspended particles will greatly reduce removal efficiency as bacteria will be more easily concealed from the UV radiation (Bitton 1994).

2.3.3.3 SODIS

Solar Disinfection is a technique promoted by the WHO and a number of organizations worldwide as an appropriate, low-tech alternative to chlorination or other more sophisticated, energy intensive disinfection methods. It consists of exposing contaminated water in conventional PET bottles to several hours of direct sunlight. Studies have been performed at least since 1984 (Amin & Han 2009b), and to date around 3 million people are supposed to be using some form of SODIS in over 30 countries for water purification (Pabon 2009). However, the literature and research so far reveal its practical use to be limited.

In the specific case of RWH, Amin & Han (2009b) analyse and compare the effectiveness of this technique with three different types of backing: reflective (i.e.

aluminium foil), transmissive (letting light through) and absorptive (black), the latter to enhance thermal pasteurization effect, which can also take place under 'strong' weather conditions (i.e. intense, prolonged sunlight, etc.). The results show the reflective backing to be more efficient overall, although for hot and sunny weather conditions, an absorptive backing (which has also been done by painting black the back side of bottles) can cause a synergistic effect between the actual heat generated (up to 50°C) and the UV-A sun rays, causing slight improvements. However, in none of the cases are total and faecal coliforms *completely* removed. The study concludes with the disheartening statement that "*SODIS seems to be ineffective for complete disinfection… even at strong weather conditions*". Notwithstanding, the same authors perform another study for a technique named SOCO-DIS that considerably enhances performance, by placing the plastic bottles inside a simple solar collector that greatly concentrates the incoming solar rays. Increases in the reduction of bacterial counts are achieved by up to 30%, as compared to conventional SODIS (Amin & Han 2009a). It is observed that lower pH values, as normally found in rainwater, also increase disinfection efficiency.

Turbidity is another factor, along with sunlight intensity, that determines whether SODIS will be effective. Higher turbidities tend to interfere with UV radiation, the same as occurs with UV treatment using artificial sources. Another issue with that technique is that of recontamination. Even if complete disinfection were to be achieved under direct sunlight conditions, total coliform counts can 'return' after a few days, especially with higher pH values and higher turbidities. However, a study performed by Meera and Ahammed (2008) showed the technique to be effective with no short term recontamination, but under strong sunlight conditions (>500 W/m2) and moderate turbidity. The danger of recontamination is also lessened with the improved solar collector technique (Amin & Han 2009a), where light is apparently shown to have a temporary 'residual' effect (possibly absorbed by water molecules or other particles suspended in water). This phenomenon is studied in more depth by Kagan (1993).

Claims by SODIS advocates, such as the well-meaning Swiss Federal Institute of Aquatic Sciences and Technology (EAWAG 2010), state that the technique can achieve "clean drinking water" in only 6 hours. However, the abovementioned studies (2009a, 2009b), performed in Korea, use 9 hours of exposure, and even then don't guarantee 100% pathogens removal. In other parts of the world the technique has been amply implemented and tested, again showing controversial and limited efficacy (Pabon 2009). In a research study performed in Mexico, considerable improvement was achieved by using titanium dioxide (TiO2) films immobilized with gel over glass cylinders. In this case, bacterial regrowth did not appear after 7 days of testing, and a complete elimination of faecal coliforms was achieved with only brief exposure on a sunny day (Gelover et al. 2006).

Finally, there is the issue of the bottles themselves. Contrary to common belief, two independent studies on the release of contaminants from the PET bottles, after prolonged exposure to sunlight, revealed no adverse health effects nor any chemical release (namely plasticisers DEHA and DEHP) above that found on normal drinking

water bottles (Schmid et al. 2008; Wegelin et al. 2001). Photoproducts were generated, as would be expected with plastics reacting to sunlight, but these occurred only on the outer surface of the bottles (Schmid et al. 2008). Evidently, more research needs to be carried out to completely assess the safety of SODIS.

2.3.3.4 Ozone

Ozone or trioxygen (O3) is a powerful oxidant and disinfectant. Its effectiveness in removing bacteria and virus from water is superior to that of chlorine. Highly resistant protozoan cysts are also inactivated in relatively short contact times. It acts by producing free radicals which affect the permeability of bacterial cell walls, as well as disrupting enzymatic activity and DNA formation (Bitton 1994, p.274, p.126-128).

Small units for water purification are widely available, but they usually require complex recirculation pumps and dosing mechanisms to be evenly spread in the water. Furthermore, ozone will evaporate out of the treated water in a few minutes, leaving no residual, and thus requires constant reapplication, with the added expenditure of energy and maintenance costs (Campbell 1983, pp.140-141). In rural communities that lack a reliable electricity supply, it might not be a viable option, since the population would be placed at risk, with no disinfection residual in the tanks or distribution systems, during a power outage.

Ozone is also not free from DBPs. Aldehydes and carboxylic acids, among other compounds, are formed when ozone reacts with dissolved organic matter in the water. Among these are formic, acetic and oxalic acid, which have been found in high concentrations following ozonation (Xie 2004, p. 19-20). Some studies suggest that water treated with even a small dose of ozone (1 mg/l) may show an increase in mutagenicity (Bitton 1994).

As in the case of most disinfectants, ozone is more efficient in clear water with low turbidities, without heavy metals or compounds that react with it, leaving less substance free for bactericidal action. However, it can also be used as a form of pre-treatment, precisely to oxidize organic matter or remove certain contaminants before filtration or final disinfection.

2.3.3.5 Silver

In this context, silver ions are proposed as an effective method for achieving water quality in rainwater collection systems. The use of silver is widespread and dates back at least 2,000 years. It has been proven to be an effective biocide, attacking a wide range of microorganisms, with no observed toxic side effects on humans, as long as concentrations are kept within an adequate range (Landau 2007).

There are two main methods in which silver is currently applied for drinking water treatment: colloidal and ionic. The former is a stable form, usually nano-particles attached to a media, where disinfection is achieved by contact or by diffusion of metal ions into the water. The second method consists in the direct release of silver ions by electrolysis, sometimes in combination with copper, which is also a known algaecide

and disinfectant, although to a lesser extent than silver. The positively charged Ag+ ions remain in water for extended periods of time, until reacting with microorganisms or precipitating with other chemicals, effectively covering the entire volume to be treated, due to the natural propensity of equally charged ions to repel each other and 'spread out' along the liquid media (Lenntech 2009).

Although silver's healing properties had been known since ancient times, it was the Swiss biologist Karl Wilhelm von Nägeli (1817-1891) who first investigated and compiled some of the bactericidal properties of the metal. He coined the term 'oligodynamic', referring to a dynamic force that's effective in small quantities (Greek – olygos). Nägeli noticed that a piece of silver in a petri dish with a culture medium would create a colony-free zone around it, without losing any volume or weight. It is now known that there is an actual loss of material in the form of ions, but was too small to be noticed at the time (Landau 2007).

There is abundant literature and patents related to the use of silver ions for a number of applications. A large number of major hospitals in the USA and Europe have successfully installed copper-silver ionisation systems to control *Legionella pneumophila*, a bacteria that grows in hot water distribution systems, as well as other nosocomial infections (Khaydarov et al. 2004; Stout & Yu 2003; Lin et al. 2011; Cachafeiro et al. 2007). Silver-copper ions have also been tested in combination with free chlorine to inactivate *L. pneumophila*. Concentrations of 400 µg/l for copper and 40 µg/l of silver were applied with varying amounts of chlorine, showing faster inactivation rates with lesser amounts of chlorine (Figure 2.2). These are the recommended concentrations set out in the UK Approved Code of Practice for the Control of Legionella (Health and Safety Executive 2000, p. 50). A synergy has also been observed between the three elements, with better disinfection efficiency as compared to either of them acting alone (Landeen et al. 1989). However, an excess of chloride anions will diminish the available amount of silver, which will precipitate as insoluble silver chloride compounds. A maximum limit of 500 mg/l chloride has been suggested if silver is to be used effectively (Landau 2007).

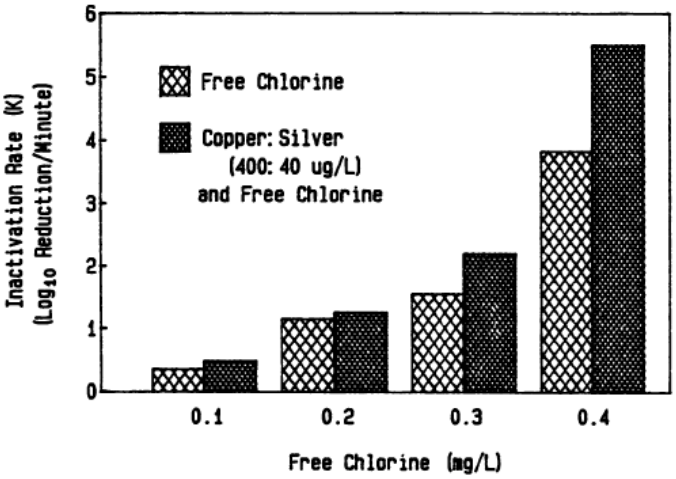

Figure 2.2. Inactivation of L. pneumophila combining copper/silver ions (400 and 40 µg/l) and free chlorine (Landeen et al. 1989)

2.3.3.5.1 Disinfection Mechanism

Positive Ag+ ions, once released into the water, are attracted and adsorbed to the negatively charged cell membranes of microorganisms. Damage is subsequently caused to the permeability of the cell wall, affecting the organism's ability to uptake nutrients. At higher concentrations, the metal ions may also form complexes with other elements which allow them to pass the charge barrier of the outer membrane, much in the manner of a 'Trojan horse'. Once inside the cell, the ions are released from their ligands, possibly by a change in pH, and attack DNA, RNA or enzymatic sites (Gerba & Thurman 1989). Silver ions can also act upon cell membranes or viral capsids, in the case of viruses, by exchanging with other existing metal ions such as Ca^{2+} or Zn^{2+} (Landau 2007).

The disinfection efficacy depends on a number of factors:

1. **Concentration.** This is affected by water flow, volume, and by the amount of silver ions being released into the water, for instance, by an electrolyser. It is suggested that concentrations between 10-50µg/l should be sufficient for bactericidal and virucidal action in drinking water; with amounts as high as 80µg/l only recommended for more contaminated untreated water (Landau 2007). A 4-year study in a German hospital revealed that *L. pneumophila* was significantly reduced with much lower concentrations (around 10µg/l), although bacteria seemed to develop a resistance to silver and require higher dosages in subsequent years (Rohr et al. 1999).

2. **Conductivity**. It is hypothesized that the higher the conductivity, the better the efficacy of silver ions, since they will be electrically transmitted faster throughout the water, and will thus be more likely to react with the microbial cell membranes. This, however, is hindered if the conductivity is related with reactive species (i.e. anions that will react and precipitate with the positively charged ions), or hardness, in the form of calcium or magnesium carbonates that will eventually adhere to the electrode surface, causing scaling and diminishing the release of silver (Landau 2007; Lenntech 2009). More research is needed in this regard.

3. **pH**. The disinfection efficacy of copper ions seems to be highly sensitive to pH variations. A study in an Ohio hospital shows that with pH values approaching 9, in both experimental and on-site tests, a copper-silver ionisation system failed to completely inactivate *Legionella spp.* while an adequate (million-fold) reduction was achieved at neutral pH. Although this held true for copper ions being tested alone, results for pure silver revealed that the latter had the same million-fold reduction efficacy for different pH values (Lin et al. 2002). This same study tested the effect of varying levels of hardness, dissolved organic matter and bicarbonates with similar results. The only parameter that seemed to reduce the bactericidal effect of silver seemed to be the presence of excess chloride ions, as detailed above.
In a different study on the absorbance of silver to proteins, results show a very low pH to also be counter-productive, since silver ions will compete with hydrogen protons, which can adsorb to similar sites (Landau 2007).

2.3.3.5.2 Bacterial Resistance

Certain strains of bacteria have been observed to develop a progressive resistance to silver or copper ions. The mechanisms for this are complex and involve genetic mutation so as to increase production of metal-binding proteins (Lansdown 2006), or the release of sulphides which precipitates metal ions. This phenomenon has been observed in *Salmonella spp.* and *Proteus mirabiles* . *Pseudomonas* and other bacteria were found alive and well in silver mines, passing on genetically encoded plasmids for silver resistance (Silver 2003).

Biofilms have also been shown to develop resistance to metal ions, in particular to copper, possibly due to similar mechanisms as described above (Lansdown 2006; Landau 2007). In the case of silver, evidence is contradictory. Shih & Lin (2010) concluded through experiments that copper-silver ionisation is effective for reducing biofilms and planktonic microorganisms such as *Pseudomonas aeruginosa,* although the study used bacterial populations which are younger than those found in real pipes. Silvestry-Rodriguez et al. (2008), on the other hand, found that silver ions are ineffective against biofilms tested on both stainless steel and PVC surfaces. Silver ion concentrations are dosed in the order of 100µg/l, and yet it is noticed that the outgoing effluent contains only 14 to 20µg/l, suggesting that the biofilm is in fact absorbing the ions among its many complexes. It is believed that if this capacity is exceeded by applying higher dosages, the biofilms could in fact be reduced.

Silver-resistant *E. coli* isolated from burn wounds treated with silver nitrate, a common hospital disinfectant, also exhibited a five-fold reduction in silver absorption or retention, a trait passed on genetically (Silvestry-Rodriguez et al. 2008). However, overall mutation and resistance to silver is considerably lower than in most antibiotics (Gerba & Thurman 1989).

Different species exhibit varying degrees of tolerance. In general terms, gram-positive microorganisms, due to their thicker outer layer, will exhibit more resistance to metal ions (Landau 2007). Protozoans and bacteria spores, as is the case with chlorine and most disinfectants, require much higher dosages to be completely inactivated, up to 20

ppm according to studies performed in *Entamoeba histolytica* (Newton & Jones, cited in Gerba & Thurman 1989).

2.3.3.5.3 Health and Toxicity

There is great controversy as to the toxicity and effect of silver ions in health and the environment, although most of the research so far highlights the fact that, in the doses normally used for water disinfection, no noticeable side effects are reported (Lansdown 2006).

"Silver and its compounds are far less toxic to humans, than most of the other heavy metals… Whereas even very small amounts of silver can act to kill microorganisms, such concentrations (0.01-0.1mg/l) are harmless to the human organism" (Landau 2007).

The reactive silver ions rapidly convert in the body to insoluble species such as silver chloride. Most of these are eliminated by the body, without being absorbed by the digestive tract. Only in long term exposure to high amounts, as in the continuous ingestion of silver salt or colloids, will silver bio-accumulate and manifest as a condition known as Argyria, causing a pigmentation of the skin. The disease has not been found to be a major cause for concern, other than the skin colouring, and only occurs at accumulated values close to 1.0g (while the concentrations used for purification are in the µg range). In cities such as Atlanta and Denver, where naturally occurring silver can be present in water supplies in ranges from 200-300 ppb (possibly due to mining activities or presence in groundwater sources), no mutagenic or otherwise adverse health effects have been reported (Landau 2007).

A study monitoring the presence of ionic silver in blood serum using an Ion Selective Electrode (ISE) showed that the ions were very short lived, with a half-life of about 7.8 seconds, apparently reacting with the large amount of chloride ions present in the blood stream. The insoluble silver chloride is eliminated by the kidneys and expelled through the urine (Silver Colloids 2010).

As far as regulations are concerned, there is also much debate and a lack of sufficient evidence. The USEPA puts a limit of 100 µg/l concentrations of silver in drinking water while Germany places a maximum of 10 µg/l in treated effluents, which is the analytical detection limit, making disinfection devices using silver ion technology very difficult to market. However, after much revision, the metal was reclassified from 'toxic' (with no substantiated evidence) to 'undesirable', with a maximum of 80 µg/l permitted exclusively for bactericidal applications (Landau 2007, p.33). German regulations have been extended to the EU Potable Water Guidelines. On the other hand, the USEPA classifies silver only as a Secondary Standard, with the only cause for concern being 'cosmetic', while placing a strict limit on copper of 1.3 mg/L (USEPA 2011), another widely used metal-based disinfectant. The Mexican Health Department, in the latest revision of its drinking water standards, has introduced ionic and colloidal silver as acceptable forms of water purification, with no specified concentration limits for application (Secretaría de Salud 2000).

In environmental terms, more stable forms such as silver salts are considered a threat above threshold amounts, particularly to some widely consumed fish, including trout. It is yet to be determined how much is the contribution of silver and how much of the other elements to toxicity (Landau 2007).

2.3.3.5.4 Colloidal Silver

A wide range of products in the market claim to have healing effects based on colloidal silver. Its use in homeopathy and other 'alternative' forms of medicine is widespread. Some of these have been substantiated and many have not. A colloidal silver preparation in Germany, for instance, has been authorised and endorsed as a product that can help relieve diarrhoea and gastritis (Landau 2007, p.22). Anti-parasitic properties have also been ascribed to similar medications. On the other hand, a study testing three different concentrations of colloidal silver on a host of pathogenic and non-pathogenic microorganisms, found no significant reduction or antibiotic effect (van Hasselt et al. 2004). This is certainly not the case with free silver ions, which are powerful disinfectants, as discussed in Section 2.3.3.5.

In the water purification realm, colloidal silver has been successfully applied to clay to increase the bactericidal properties of conventional ceramic filters. Oyanedel-Craver & Smith (2008) tested these filters for removal of indicator bacteria, concluding that colloidal silver, applied as a paint, enhanced the disinfection efficiency of ceramic with pore sizes from 0.02 to 15 µm. Silver concentrations in the effluent filter water were initially greater than 100 µg/l, but dropped considerably after a few hours of operation. The authors conclude that *"colloidal-silver-impregnated ceramic filters, which can be made using primarily local materials and labour, show promise as an effective and sustainable POU water treatment technology for the world's poorest communities"*. More recently, the use of porous ceramic combined with silver nano-particles has also been successfully tested, with a more controlled release of ions and high disinfection efficiencies ((Lv et al. 2009)

An NGO operating mainly in Nicaragua, has been using filters such as these for more than a decade, prepared with local potters at a relatively low cost (Potters For Peace 2010). Their designs and ideas have been exported to many other developing countries, and were exhibited in the IV World Water Forum held in Mexico City in 2006.

The Katadyn filter, developed in Switzerland over 50 years ago, is based on the same principles. Although efficacy has been assessed for bacteria, elimination of viruses is not guaranteed (Davies & Etris 1997). Ceramic filters have improved over the years with new techniques and greater efficiencies due to reduced pore size. Silver in different forms is seen as a durable and cost-effective method for enhancing performance (Bettin et al. 2013).

2.3.3.5.5 Silver compounds and nano-particles

Although the present study is based on the use of silver ions as a purification method,

it is worthy of mention that a number of compounds including silver have been used for centuries, and new forms are constantly being researched.

Silver nitrate is a well known disinfectant agent used in hospitals to treat wounds and burns. Silver sulphadiazine is a cream which is regularly used in the control of yeasts such as candida and various fungi (Landau 2007, p.24). Activated carbon filters impregnated with silver nitrates are commonly sold, to protect the carbon fines from colonization, although the silver will be depleted if excess turbidity or reactants are present, such as organic matter, chlorine, iron or sulphur, which will cause it to precipitate (Campbell 1983, p.140). It must be noted, however, that silver chlorides break down in the presence of light, releasing chloride gas and freeing silver ions, which may potentially recover part of the disinfection capacity of the substance. More research is required in this area.

Impregnation of a number of materials with silver nano-particles is a new and developing area of research. Ultrafiltration membranes modified in this way have been shown to increase efficacy in the removal of a number of microorganisms, including virus (Zodrow et al. 2009). Silver also has the capacity to store large amounts of oxygen by adsorption, due to its physical configuration, which makes it attractive also as a powerful oxidant for a variety of applications (Davies & Etris 1997). Methods are also being developed to synthesize nano-particles using bacteria and fungi, in an eco-friendly and reliable way (Botes & Cloete 2010). Finally, it must be noted that the ultimate objective of any silver complex (in the case of water purification) is to release silver ions into the water. The idea of using nano-particles is to optimize the ion delivery of such ions, transport them to the precise targets in the right amounts. This phenomena is known as sustained release, and is a subject of much investigation (Pradeep 2009).

2.3.3.5.6 Applicability to RWH systems

In summary, silver ions offer a viable option for water treatment in RWH systems. The main advantages are (Lin et al. 2002):

- Reduced dependence on external factors such as temperature (in contrast to chlorine and UV that are affected by high water temperatures).
- Little or no formation or known harmful by-products.
- Easy installation and maintenance, compared to ozone, for instance.
- Leaves a residual disinfectant for long periods of time, making it ideal for cistern water conservation throughout dry seasons.
- No demonstrated health or toxicological effect in the amounts required.
- Silver electrodes can be combined with copper to increase efficacy and lower costs (since copper ions will target different parts of the cell, as well as other organisms such as algae, there can be a synergistic effect). This, however, may have issues with local regulations, particularly in the EU, where there is a current controversial ban on copper (not on silver) for drinking water (Health and Safety Executive 2013).

2.4 REVIEW OF TESTING METHODS FOR WATER QUALITY

Small scale, rural water supply projects, whether they are based on rainwater or ground sources, pose specific challenges for quality monitoring, as compared to urban, largely centralized systems. This is mainly due to their geographical dispersion and, at times, difficulty of frequent access, which in turn implies higher monitoring costs (Lloyd & Helmer 1991). Issues such as the vicinity of certified labs to analyse samples, and the time and effort taken to transport these, have to be considered. In many cases, field labs have to be set up, and compromises be made in terms of what parameters are truly indispensable to be measured. The WHO recognized the complexities involved during the early years of the International Drinking Water Supply and Sanitation Decade, from 1980 – 1990, which held the speculative promise of 'completely eliminating all lack of adequate access to drinking water' in a mere decade (Hemson et al. 2008, Ch. 1). Thus a specific set of guidelines: "Drinking Water Quality Control in Small Community Supplies" was released in 1984. This has been revised and updated since (WHO 1997).

What follows is a brief review of some of the methods available for monitoring water quality, including those that can be successfully applied in fieldwork.

2.4.1 CHEMICALS AND SILVER IONS

2.4.1.1 Spectrophotometry

The most common method for analysing chemical substances is spectrophotometry in the UV-Visible light range (also known as UV–visible spectroscopy), related to the colour or wavelength absorbance of a substance. Older versions of the 'Standard Methods' had a procedure for determining silver concentrations in water using dithizone and a standard spectrophotometer. This, however, is not included in the latest editions, and is suggested only when no other suitable methods are available (APHA 2005, 3500-Ag). The recommended options are atomic absorption spectrometry (AAS) or inductively coupled plasma (ICP). Electrothermal atomization is presented as the most sensitive method for natural waters (APHA 2005, 3113B). Samples need to be acidified to pH<2, ideally with nitric acid (HNO3) at the time of collection, and analysed as soon as possible.

An ICP source consists of a flowing stream of ionized argon gas. The sample is 'nebulized' into the plasma chamber reaching temperatures between 6000 and 8000 K, which will almost completely dissociate molecules, thus allowing the measurement of single constituent elements.

There are two types of ICP:

- Optical Emission Spectrometry (ICP-OES) uses the intensity of the electromagnetic radiation of the sample element to obtain a reading. Silver can be measured down to 7

µg/l, at a suggested wavelength of 328.07 nm. The upper limit is 50 mg/l (APHA 2005, 3120B).

- Mass Spectrometry (ICP-MS) will generate charged molecules by ionisation and then use their mass to charge ratio to determine measurements. Much lower concentrations can be obtained with this instrument, down to the ng/l level. In the case of silver, detection limits are as low as 0.003 µg/l (APHA 2005, 3125B), making it the ideal method for silver measurements.

For faster determinations, commercial kits are available using standard UV-Visible Spectrometry, with detection limits down to 5 ppb, using a cadion 2B indicator, which does not have as many interferences as the traditional dithizone method. The indicator will form a coloured complex with silver ions at higher pH values, with an absorption peak of 560 nm (Fu-Sheng 1983). Samples which have been stabilized with nitric acid need to be adjusted to a pH of 9–10, with 5.0N Sodium Hydroxide, according to the method. This technique, though quite reliable up to 700 ppb, is not suited for very small concentrations or very accurate measurements, given the 5 ppb detection limit (Hach Company 2003).

Known interferences in both the cadion 2B and the dithizone method are most heavy metals, ammonia and chloride, which will precipitate silver ions. Care must also been taken to not contaminate samples, such as with a pH meter, due to silver contamination from the electrodes. It is suggested in most methods to regulate pH for preservation using standard strips rather than metallic electrodes.

2.4.1.2 Ion Selective Electrodes

The Ion Selective Electrode (ISE) consists of a sensitive electrode that will allow only a specific ion through, depending on its structure, and convert its activity in the solution to an electrical potential, based on a reference electrode. A pH meter is a form of ISE that selectively reads dissolved H+ ions in water. The ion selective membranes are usually made of glass, crystals or polymers, depending on the element to be tested and the sensitivity required (IUPAC 1994).

ISEs allow for quick measurements, although not as precise as the methods described above. They are commonly used for fluoride, calcium, carbonate and other anions. In the case of silver, companies such as Jenway and NICO2000, both represented in the UK, sell electrodes for this element. In these devices, the lower detection limit is reported to be around 10 ppb, but will only give reasonably precise results well above

100 ppb[4], making them inadequate for the present research project, where much lower concentrations are required.

However, a German study on rainwater cisterns in Thailand treated with a silver-based product, used a combination of Ag_2S-coated silver wire and a standard Ag/AgCl reference electrode, to adequately measure concentration ranges between 1 – 100 ppb (Frevert 1988). This innovation might be very useful for rapidly monitoring systems treated with silver ions, and ensuring they are in the right concentrations to achieve a disinfection effect.

2.4.1.3 Quick tests (colorimetry)

A rapid colorimetric test for silver is also available by some commercial lab equipment manufacturers. It uses 1,10-phenanthroline which will react with silver ions at approximately neutral pH to form a colourless, water-soluble complex. This complex, combined with Bromopyrogallol Red, forms a water-insoluble blue precipitate, which is captured on a filter and compared to a colour chart to obtain a semi-quantitative result (Hach Company 1996).

The method can read values of dissolved silver ions between 5 and 50 ppb, with an accuracy of 5ppb. It is useful to get a general idea, or to test for absolute presence/absence, but does not give very accurate results in the ranges required for the present research. It is, however, valuable as a low cost alternative to operators of POU systems using silver ions, especially in remote communities where quick readings are required.

Other methods have been investigated for these low concentrations that compare well with ICP-MS (Lerchi et al. 1996), using lipophilic chromo-ionophores (i.e. synthetic molecules which bind or transport free ions) impregnated in polymeric sensing films. Trace analysis techniques, utilising fluorescent optode microspheres, which translate their signal to a measuring instrument using fibre-optics, have also been successfully tested, including detection of silver ions down to parts-per-trillion concentrations (Wygladacz et al. 2005). Most of these methods, however, are relatively expensive and not as of yet widely available for routine analyses such as the ones that would be required in a rural development project.

[4] Technical data and information available on: http://www.nico2000.net/analytical/silver.htm#water and http://www.jenway.com/product.asp?dsl=280

2.4.2 MICROORGANISMS

2.4.2.1 Use of indicator organisms

Ideally, a microbiological analysis of any drinking water supply should be as extensive as possible, covering a wide range of pathogenic bacteria, viruses, protozoa and algae. This is, however, neither practical nor applicable in the grand majority of scenarios, particularly in the remote communities of developing countries, which barely have any monitoring at all. Thus, an indicator microorganism needs to be used, and assumptions be made depending on its presence or absence. The Standard Methods (APHA 2012) recommend at least measuring total and faecal coliform bacteria (which are mostly *E. coli*) for drinking water. However, when even this is not achievable, some authors suggest using only the faecal indicator (Lloyd & Helmer 1991, pp. 85-87), given the higher risk associated with this sub-group. The WHO guideline value is zero/100ml, so any presence is considered of concern (WHO 1997).

To this day, most international standards and guidelines, including those for surface and wastewaters, use the coliform group as a basic indicator for policy making and quality regulations. In some cases heterotrophic plate counts, which comprise a very general reading of all bacteria that will grow on a non-selective agar, are also used. These do not discriminate between organisms that can be pathogenic to those which are not, but can give an idea as to the quality or overall pollution load of the source.

2.4.2.1.1 The Coliform Group

The reasons for choosing coliform bacteria as an indicator organism over 100 years ago are complex and historical (Gleeson & Gray 1996). The general argument goes that if these bacteria are found, then most likely other less resistant pathogens can also be found. Another argument in favour is their ease of incubation and detection, due to their ability to ferment lactose, along with the relatively low cost of modern standard tests. Faecal coliforms, on the other hand, grow in the intestines of warm-blooded animals, so their presence will usually denote faecal contamination. *E. coli*, the major component of faecal coliforms, is also used as an indicator nowadays.

Despite its common adoption in almost all water regulations worldwide, including Mexico (Secretaría de Salud 1994), the Coliform group has come under attack as a viable indicator for a number of reasons, namely: (from Gleeson & Gray 1996, p.44)

- Regrowth in aquatic environments and water distribution systems
- Not necessarily indicative of a health threat
- Lack of correlation with other pathogen numbers, such as protozoa or virus
- Protozoan cysts and some viruses more resistant to common disinfection methods (Bitton 1994, p.113).

Alternative or parallel indicators such as enterococci (see below) and Clostridium, which is highly resistant in the environment, have been proposed with limited success, mostly due to the high costs associated with implementing additional indicators. The

added health benefits relative to the investment required is still under evaluation (Edberg et al. 2000).

In summary: “Simple indicator systems such as faecal coliform measurements may prove to be inadequate for determining microbial risks associated with consumption of water from rainwater catchment systems”. (Lye 2002)

2.4.2.1.2 Faecal Streptococci

Faecal streptococci are a group of Gram-positive cocci, belonging to the genera Enterococcus and Streptococcus, the latter more predominant in animal excreta (i.e. Str. bovis and Str. equinus), while the former are more indicative of human faeces (Ent. faecalis, Ent. faecium). Their use as an indicator dates back to the early 20th century. Among the advantages are their greater persistence in the environment, including higher resistance to chlorination, while at the same time the fact that they rarely multiply in water (Gleeson & Gray 1996). It must be noted that coliforms do reproduce in water, making sample storage and counts more complicated, thus the greater need for rapid, refrigerated transportation to a lab after sampling (APHA 2012).

A study by Evans et al. (2007) suggests that enterococci might be a better indicator of health risk than *E. coli* for rainwater quality monitoring, due to their greater persistence in the samples analysed (where most pollution was from animal origin), noting that pathogens such as Campylobacter have been found in rainwater with no correlation to faecal coliform counts.

The ratio of faecal streptococci to faecal coliforms (FC/FS) has long been used as a means of detecting the origin of contamination on a water source. A ratio greater than 4.0 would imply pollution from human excreta, while less than 1.0 gives strong evidence of animal origin (Meera & Ahammed 2006). This, however, has been widely contested by a number of authors (Gleeson & Gray 1996, pp.107-108). The ratio is only valid in the first few hours after discharge, given the variable rates at which the bacterial groups multiply, and even then research has found results to not be constant nor reliable in all cases.

Despite reluctance from labs or existing authorities to add an additional indicator, faecal streptococci has made it into the EU Drinking Water Directive since 1995, and is being considered as secondary test, but not a replacement, for *E. coli* monitoring in the USA and elsewhere (Edberg et al. 2000).

2.4.2.1.3 Viral bacteriophages

Bacteriophages are virus that infect bacteria, and can be classified depending on which species they attack. Somatic coliphages are of more interest for the present research, since their host bacteria (*E. coli*) can be commonly found in RW, in aerobic environments (Kutter & Sulakvelidze 2005). Another strain, known as MS-2 coliphage, has been tested against silver ions (Kim et al. 2008). Phages have been successfully used as indicators of water quality (Hilton & Stotzky 1973; AWPRC

1991), and compared against the more conventional coliform indicator, with advantages such as greater resistance, relative ease of detection (4 hour incubation period instead of 24 h) and the possibility to model potentially pathogenic viruses (Grabow 2001; Jofre et al. 1995).

2.4.2.2 Methods for analyses

One of the main aspects of coliforms is their ability to produce acid and gas in lactose-based media. Both of the most well known methods, multiple-tube fermentation (also known as Most Probable Number or MPN) and Membrane Filtration (MF) rely on this ability. It must be noted that coliforms are not a formal taxonomic unit, but are grouped together by detection characteristics such as these, which make them convenient as an indicator microorganism (Gleeson & Gray 1996).

2.4.2.2.1 Most Probable Number

The method was first developed in 1915, and is based on the dilution of the sample into successive test tubes, observing gas production due to lactose fermentation in each one, until no more gas is produced (i.e. no bacteria detected). In this manner, a statistical estimate can be achieved. This stage, called the presumptive test, will be achieved by incubating at 37°C up to 48 hours in a lactose based medium. Positive tubes then need to be sub-cultured on an adequate medium in what is known as a confirmatory stage. A similar procedure exists for *E. coli* (APHA 2012).

The test is lengthy, time-consuming and not entirely accurate. However, many water quality regulations still require it, probably due to its low cost and relative simplicity, as well as a general resistance to change standard, established procedures. A modification of the technique is available for simpler presence/absence tests (Gleeson & Gray 1996, pp.84-85).

2.4.2.2.2 Membrane Filtration

In most of the literature reviewed above, the preferred method for detecting bacteria is membrane filtration. This was developed in the 1950s as an alternative to the MPN statistical method. It consists of filtering the sample through as filter with sufficiently small pore size so as to retain bacteria, and then aseptically transferring into a petri dish with a selective agar base or medium, depending on the type of microorganism sought (Gleeson & Gray 1996, p.70). The conventional method stated that total coliforms were to be incubated 35°C for 22-24 hours on LES_ENDO agar or m-ENDO medium, and *E. coli* at 44°C for roughly 24 hours on m-FC medium or similar (APHA 2012). Modern media and techniques, such as the Colilert system (Standard Method 9223B), approved by the USEPA in the 1980s, and the more recent m-Coliblue 24® method, allow to measure total coliforms and *E. coli* at the same time, based on a colour differentiation of the growing colonies. Incubation is only 24 hours at 35°C, saving time and effort in doing both tests at the same time (Gleeson & Gray 1996, p.87). The m-Coliblue 24® method was approved by the USEPA in 2006, and

is now accepted worldwide as a reliable method for detecting these indicator bacteria (Crane et al. 2006).

A rapid test was also developed for faecal coliforms in 1979. It utilizes a buffered lactose medium with a sensitive pH indicator. Colonies will turn yellow against a purple background after 7 hours at 44°C incubation (APHA 2005). All of these procedures have been compared favourably to previous techniques such as MPN and older membrane filtration techniques. Similar commercial kits are also available for other bacteria such as Enterococcus (Gleeson & Gray 1996, p.91,106). The procedure for analysing Faecal streptococci is similar to that of coliforms, with incubation at 37°C for 48 hrs.

2.4.2.2.3 Heterotrophic Plate Count (HPC)

HPC consists of a general count of all viable bacteria in drinking water, which is useful to get a better idea as to the efficiency of treatment processes. It is a known fact that the presence of bacteria in purified water does not necessarily imply pathogenicity (Landau 2007), so small numbers are expected even in thorough filtration and disinfection systems (Jordan et al. 2008). The Standard Methods contain a procedure for measuring HPC based on incubation on a non-selective agar for several days (APHA 2005). It is thus not practical where quick interventions and measurements are needed.

A faster technique has been developed and tested to have consistent results with conventional methods. The procedure uses the quantification of ATP with a bioluminescence assay, based on the reaction between the luciferase (enzyme), luciferin (substrate), and ATP. Light is emitted during the reaction and can be measured, correlating it with the ATP quantity extracted from bacteria. The technique can be done on-site, with a small sample (0.1- 20ml) and is cost-effective compared to other methods (Lee & Deninger 2001). More research is yet to be done on this technique before enters mainstream testing procedures.

2.4.2.3 Inoculation

In order to adequately test the efficacy of any filtering or purification systems, it is a common practice to artificially increase or ‘spike’ the number of microorganisms in the initial sample. Rainwater in particular may contain a relatively low count, given the dilution that occurs with large precipitation volumes. A good efficiency analysis requires enough initial numbers to test the true removal rate of a filter or disinfection mechanism.

Research studies for POU devices involving ‘spiking’ may include bacteria or viruses. A good example of this is Jordan et al.'s study (2008) for testing a conventional filter and UV system in household rainwater cisterns. Here the original cistern sample was spiked with *E. coli* (ATCC #25922) to a total concentration of 105 CFU/ml, and MS2 bacteriophage (ATCC #15597-B1) to 105 PFU/ml (plaque forming units). The inoculation is done by diluting and mixing a stock of known concentration with the

sample. Tests may need to be performed rapidly after inoculation to prevent bacterial die-off in the absence of sufficient nutrients.

The type of indicator bacteria used is important in these tests. Even though the goal is to measure the extent of pathogenicity, it is ideal to do so minimizing risks of exposure to lab analysts. A number of strains or genomic varieties can exist within a given species. *E. coli*, for instance, includes the rather pathogenic O157:H7 as well as the harmless K12 strain, which is commonly used for laboratory research (Schaechter et al. 1999, p.129).

2.4.2.4 Polymerase Chain Reaction (PCR)

Polymerase Chain Reaction (PCR) is a technique for determining the identity of organisms being analysed by creating multiple copies of target DNA using an enzyme. It has been shown to be an accurate and highly sensitive method for detecting bacteria, viruses and protozoa in water (Toze 1999). Although it is a quick and reliable method, it is not without limitations. Microorganisms that might be already dead can also be detected, if their DNA is intact, giving false positives. The cost and training required are also factors to consider.

It has been used successfully for detecting and accurately quantifying the number and occurrence of pathogenic bacteria in rainwater tanks. In a study in Australia, 27 rainwater cistern samples were analysed using PCR for *E. coli*, *Enterococci*, *Clostridium, Campylobacter, Salmonella* and *Giardia*, among other microorganisms (Ahmed et al. 2008).

2.5 SUMMARY

The literature review has highlighted the following points, which are most relevant to the research and methodology described in this thesis:

- The San Miguel de Allende area has several concerns related to water, including a lack of adequate supply to rural communities and quality issues, notoriously fluoride, in the sites where RWH systems are being monitored (2.1).

- Rainwater collected directly from rooftops is observed to be not fit for drinking in many cases, posing a health hazard unless adequately treated, due to a variety of factors, including chemical and biological causes (2.2).

- A number of filtration and disinfection methods are commonly used worldwide to purify rainwater (2.3), with silver receiving relatively little attention in the literature, despite being shown to be a relatively safe and powerful disinfectant in the treatment of waters from other sources (2.3.3.5), highlighting the importance of the current research project.

- Testing and laboratory methods were covered in section 2.4, with the most relevant for the present work being mainly:

a) Spectrophotometry for silver ions (2.4.1.1)

b) Coliforms as a bacterial indicator, despite the limitations and controversies covered in section 2.4.2.1. The preferred method chosen for analysis, due to its convenience and availability in the lab was membrane filtration (2.4.2.2)

c) Bacteriophages as a viral proxy. Methods used and a discussion on this emerging technique were covered under the corresponding heading in section 2.4.2.1.

d) Microbiological inoculation methods, considered an important part of the laboratory work, were described in 2.4.2.3.

- Other testing techniques and treatment methods, not necessarily utilised for the current dissertation, have been cited for the sake of reference and comparison.

Building up on this review, the following chapter provides details on the methodology actually used both in the field and in the laboratory throughout the research project.

3 METHODOLOGY

3.1 INTRODUCTION

The project at large consisted of two major components: fieldwork, which was done on two different periods (2010 and 2012), and laboratory experiments, carried out mostly in the Environmental Engineering Lab at UCL. It was not possible to do an exact replica in the lab of the systems of the field, due to an incompatibility of connecting components between Mexican and European standards, as described in Section 3.3.1.1. However, the prototypes set up emulated inasmuch as possible, within the additional obvious restrictions of space and sizing, the basic operation of the systems. It was also possible to bring into the UK the same silver ioniser and electrode devices as were used in Mexico; while most of the standard filtering components were similar enough to those installed in the field, making the model suitable for an adequate simulation.

Given the wide range of parameters that could be tested and evaluated, along with the cost of analysing certain components (particularly silver), it was decided that the project would focus on *qualitative* results rather than quantitative. Evidently, it would have been ideal to take numerous repeated samples in a specific community or model, obtaining excellent statistical data, but that would have implied taking fewer observations from other systems which could provide added valuable information. The author would like to argue that there is nothing inherently wrong in either approach. One could potentially focus on only one or two sites, for instance, and build an entire research out of a very thorough evaluation of a handful of variables with a consistently large sample size, but it would have the danger of missing out on a greater picture. In an emerging field such as the scientific quality assessment of rainwater harvesting systems, and more specifically with regards to the novel applications of silver ions, it was considered best to look at the general panorama, hinting at trends and possible results of different scenarios, rather than focusing on obtaining extensive quantitative data of particular aspects.

3.2 FIELDWORK

3.2.1 SITE DESCRIPTION

Out of the 14 systems originally installed from 2007 to 2009 in San Miguel de Allende, a selection was made on each fieldwork period as to which ones would be studied. One of the installations was a residential system, and was thus discarded as a valid site for comparison, and another two had been dismantled for relocation by the community, being unavailable throughout the entire project duration (see discussion on 6.4). That reduced the number of viable options to 11 sites, all in communities within the perimeter of the San Miguel de Allende municipality, located across 10 rural primary schools and one health clinic. The corresponding details for the selected sites are described in Table 3.1.

The two sampling rounds took place in 2010 (Apr – Jun), and 2012 (Sep – Oct). In theory, the first period was considered the dry season and the second wet or rainy. As explained below, possibly due to climate change, this was not the case. Though it would have been ideal to sample all 11 systems in both periods, this was not possible due to a number of limitations, mainly:

a) Rainwater storage: Some of the systems were being repaired or maintained and were not fully functional at all times.

b) Accessibility: Unexpected torrential storms fell in the midst of the dry season in 2010, causing several of the roads to become muddy and inaccessible, forcing the removal of planned sites form the initial sampling list. In some cases, however, this brought advantages in terms of rainwater collection, bringing up the water levels in the cisterns.

Completed fieldwork results and discussion for each round were published in distinct journals and presented at international conferences (Adler et al. 2011; 2013).

Table 3.1. Rainwater harvesting systems in Mexico used for study

				Cistern		Sampling[3]	
ID	**Community/sampling site**[1]	**Roof area** (m^2)	**Consumption** (m^3/year)	**Type**[2]	**Size** (m^3)	**1st**	**2nd**
1	Rancho Nuevo V. Guadalupe	80	10.0	TK	5	x	x
2	San Antonio de la Joya	82	11.6	OG	17	x	
3	Don Juan	49	8.0	OG	7.5	x	x
4	La Aurora	60	8.8	TK	10	x	x
5	San Miguel Viejo – Classroom	98	32.0	OG	45	x	x
6	San Miguel Viejo – Kitchen	60	16.0	UG	17	x	x
7	Augustin Gonzalez – Clinic	140	NA	UG	45	x	x
8	Augustin Gonzalez – School	350	48.0	UG	80	x	x
9	El Salitre	200	30.0	OG	17	x	x
10	Montecillo de Nieto	NA	NA	OG	30		x
11	Boca de la Cañada	140	28.0	OG	17		x

1. Systems are all installed in schools, except for (#7) which is a rural clinic
2. OG – Overground geomembrane; UG –underground cistern; TK –pre-fabricated tanks (5,000 L)
3. Refers to whether system was used or not in each sampling period (1st: 2010; 2nd: 2012)

3.2.2 SET-UP AND COLLABORATION ARRANGEMENTS

Since the author had previous working experience in the region, having been in charge of actually implementing the RWH systems between 2007 and 2009, contacts were already in place with the main stakeholders. The Municipal Government was approached for collaboration in sampling, logistics and use of laboratory. The local water authority (SAPASMA) agreed to facilitate a water quality lab, located at the municipal wastewater treatment plant, as long as some consumables were paid back or replenished. They also helped partially with logistics, at times lending a truck or an assistant for the sampling visits.

Another important source of collaboration came from the municipal Ecology Department (*Dirección de Medio Ambiente y Ecología* or DMAE), which facilitated contact with the communities, as well as supporting the project with qualified personnel, sampling equipment and transportation.

Initially, fieldwork was scheduled to start in February 2010. However, set-up of the project and negotiations involved took longer than expected, with actual sampling

starting in April. Permission was also sought from main representatives in the selected sites (communities own the systems, even though the funding comes from the Government or NGOs), who were overall greatly supportive of the project, facilitating access to the schools and sampling sites.

Funding came mostly from the Mexican Science and Technology Council (Conacyt), as the main sponsor of this PhD project. According to a prearranged schedule, the author returned to the UK in the early summer of 2010. This constraint, added to the delays discussed above and the difficult access conditions made repeated sampling of the each site a near impossibility, which would have been ideal from a statistical point of view. In consultation with the other stakeholders, it was decided in the end to collect only one sample per site, gathering as much qualitative data as possible in each case, as mentioned above.

The second sampling round (Sep – Oct 2012) was done in the field by a volunteer from EWB (Engineers Without Borders) under close supervision from the author in the UK and by IRRI-Mexico (the NGO to which he is affiliated). Due to budgetary constraints, it was not possible to travel directly, so the volunteer was briefed extensively in London on all the sampling protocols, provided with field measuring equipment and sampling containers, and supported by all the prearranged contacts on the field, in particular the lab at the SAPASMA, who also provided vehicle, assistance and logistics. Wherever applicable, refrigerated samples were sent back to London for analysis. Detailed photographs and notes were taken from the sampling sites and of any tests performed locally. Lessons learned from the first round, as well as from the lab experience, were implemented, resulting in an extra sampling point being added to the system, more duplicate/repeat tests whenever possible, and more parameters being added to the overall water quality evaluation (see 4.2.1).

3.2.3 GENERAL SYSTEM DESIGN

All RWH systems contain approximately the same components, as outlined below (see Figure 3.1):

- Gutters: made of PVC, containing a plastic 'mesh' to retain leaves, rocks, etc.

- Settling tank/First-flush: consisting of a 450 L HDPE plastic covered tank.

- Cistern: Varied according to terrain and site conditions, but mostly made of plastic geomembrane (drinking water grade)[5], built over-ground with a supporting steel mesh structure. When buried, the floor and walls were lined with geomembrane instead of concrete. On two sites (see Table 3.1), plastic tanks were used. All cisterns were covered (Figure 3.2).

- Stainless steel filter with manual backwash mechanism, removing particles>100 µm

- Two-stage filter, including a spun polypropylene and a refillable cartridge containing a mixture of GAC (Granular Activated Carbon) and KDF (Kinetic Degradation Fluxion) filtration media. Cartridges are commercially available and commonly used in Mexico for household filtration (Figure 3.3: Complete system comprising pump, filters and silver ion unit (upper right) with settling tank above enclosure).

- Silver ionising unit, connected to the same electric supply as the pump, except in one case (Site #6 on Table 3.1) where a small 5W solar panel was used. Voltage was initially set to 5V in all systems.

- Pressure pump, with capacities varying in size depending on site, typically 0.4 HP.

- Drinking fountains where purified water is dispensed to school children and visitors.

[5] Geomembrane is usually made from a variable composite of High Density Polyethylene (HDPE) and Polypropylene. Some manufacturers also use Low Density Polyethylene (LDPE).

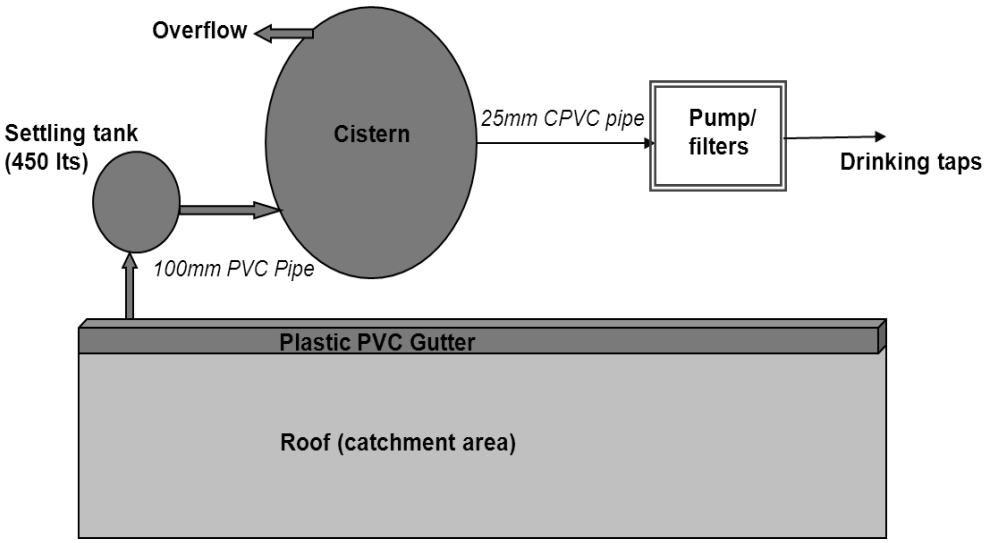

Figure 3.1: General System Design (not to scale). Silver ioniser is inside the pump/filters box

Figure 3.2: Overground cistern with settling tank and drain valve (lower right)

Collection roofs at the sites are made mostly of concrete, coated with a common asphalt-based waterproofing paint known by its brand name ‘Fester’ (manufactured by Henkel in Mexico). The only exception to this was Rancho Nuevo (site #1 in Table 3.1), which has an asbestos roof. The overall conditions of each catchment surface were found to be highly variable. In some cases the waterproof coating was intact, in others it looked worn and badly in need of repair.

There are two important exceptions to the general design described above which are worthy of mention. Sites #5 (San Miguel Viejo) and #7 (Clinic) were not equipped with silver ionising units from the outset. The first one uses an elevated 1,000 L plastic tank on the roof[6] to store and dispense treated water by gravity to drinking fountains spread across the school playground. This tank contains a pre-existing floating purification device (made of ceramic balls impregnated with colloidal silver, enclosed in a tubular PVC casing). School teachers were unclear as to when exactly it had been purchased, but presumed it had only been a couple of years before the implementation of the RWH system in 2009. Its life-expectancy was reported to be 10 years, so it was assumed for the sake of the present study that it was still fully functional, and thus able to release some silver ions into the water.

The second system mentioned (#7) was the only one operating in a clinic (instead of a school). It was among the first ones, installed in 2007, and was equipped with a reverse osmosis (RO) unit at the main drinking water point, after regular filtration, located inside the clinic. An additional tap was located right outside the clinic, for general use, without the RO treatment. In both cases, filtration was done using the same components as the other systems (pre-filtering, GAC/KDF cartridge, etc.). A floating chlorine dispenser was installed in the underground cistern (45,000 L capacity). Chlorine tablets (purchased from a swimming pool supplier's store), were supposed to have been replaced every 1 – 2 months by the clinic's staff. However, in reality this happened only occasionally (see discussion on 6.4). Silver ions were not implemented here as it was considered that the pre-installed RO and chlorination were enough to guarantee disinfection at the main drinking point, and due to budgetary constraints.

[6] This particular type of tank, known as *Tinaco*, is prevalent across Mexico. Both the tank and drinking taps were already installed when the RWH system was implemented, and thus incorporated into the design.

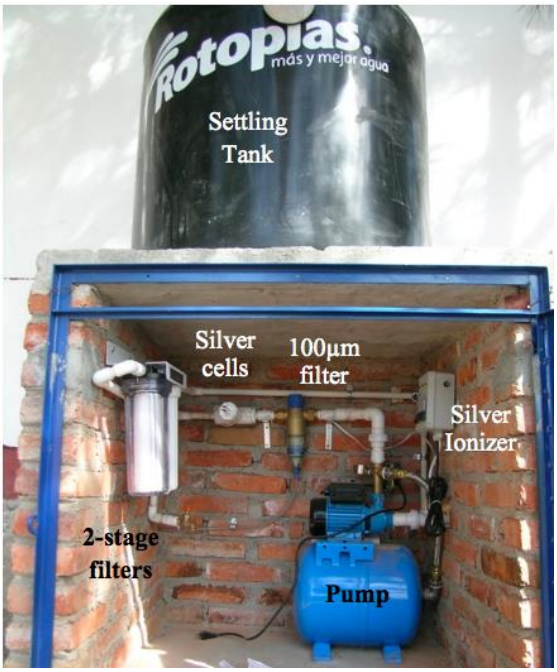

Figure 3.3: Complete system comprising pump, filters and silver ion unit (upper right) with settling tank above enclosure

3.2.4 SAMPLING

Inasmuch as possible, sampling procedures and protocols were consistent throughout both sampling periods, in order to minimise errors and be better able to compare the two data sets. In general terms, the different parameters were classified and measured as outlined below. Individual variations for each period (2010 and 2012), along with the specific sites and sampling points analysed in each case, are discussed in the corresponding sections under Fieldwork Results (Ch. 4).

3.2.4.1 Field parameters

These were measured onsite and included variables such as temperature, pH, conductivity and dissolved oxygen (DO). All of these parameters were checked again at the lab the same day, before starting microbiology tests. The methods used for each parameter are summarized in Table 3.2. Since more than 2 years elapsed between one sampling round and the other, some equipment was inevitably removed, changed or upgraded. This is also shown in the table, where applicable.

Oxygen values were found to be very similar after collection in watertight jars and transport back to the lab, compared to those read directly in the field. In some cases, due to the high cost of the sensing equipment, it was preferred to analyse DO back in the SAPASMA lab, especially when visiting the more remote communities. A visual inspection of colour and water quality was also recorded on every visit, as well as the overall condition of the system.

3.2.4.2 Local laboratory analyses

Measurements that required digestion (i.e. COD) or more sophisticated equipment were collected in sealed 250 ml glass bottles and transported refrigerated to the local lab, located at the municipal wastewater treatment plant of San Miguel de Allende and operated by the local Water Authority (SAPASMA). Microbiological samples were collected according to standard procedures (APHA 2012), in commercially available sterile 100 ml plastic bags containing a capsule of sodium thiosulfate to remove traces of chlorine that may inactivate bacteria previous to measurement. These were analysed promptly upon arrival with membrane filtration and 24 hour incubation, using the USEPA approved (Crane et al. 2006) methods described in Table 3.2. Although the use of coliform bacteria as indicator microorganisms is controversial (Gleeson & Gray 1996, see also 2.4.2), it was implemented here for convenience due to its widespread acceptance in most drinking water guidelines worldwide and to ensure a consistent bacterial measurement throughout. Availability of reagents and ease of detection were also factors to be considered.

Table 3.2. Parameters evaluated in the field/local lab (Mexico) and methods of analyses

Parameter	Equipment (2010)	Equipment (2012)
pH (*in situ*)	Orion Aplus portable PH/ISE Meter	pH strips: "pH-Fix 0-14"
pH (lab)	NA[1]	TEC Orion 420+ pH meter
Conductivity	ECTestr meter: low (0– 1900µS)	Ibid.[2]
Coliforms	Total / *E. coli* Hach m-ColiBlue24® Broth (Membrane Filtration method)	Total / *E. coli* Hach m-ColiBlue24® broth (Membrane Filtration method) Faecal Coliforms Hach m-FC broth
COD	Hach DR2800 Spectrophotometer	Ibid.
Total Hardness	Aquachek 5-in-1 Water Quality test strips	Titration according to Mexican Standard (NMX-AA-072-SCFI-2001). Reagents: Ammonia buffer solution, Erio-crome black indicator, EDTA solution (0.01M)
Total Alkalinity	Aquachek 5-in-1 Water Quality test strips	Titration according to Mexican Standard NMX-AA-036-2001. Reagents: Phenolphthalein indicator, methyl orange, sulphuric acid 0.02N
DO	Hach sensION 6 DO meter	Ibid.
Silver	Hach DR2800 Spectrophotometer	NA

1. NA: parameter or equipment not available in that particular period
2. Ibid: refers to the same equipment being used in both periods

A spectrophotometer for analysing silver was only available during the first round (2010). However, due to unexpected supplier delays, the reagents arrived too late to cover all of the samples. For the second round (2012), it was not available altogether, but by then UCL had purchased an ICP-MS which was in full operation at the time, allowing for silver samples to be analysed in the UK (see below).

3.2.4.3 UCL lab analyses

Two sets of samples were collected at selected sampling points for shipping back to the UK, with the purpose of performing more in-depth analyses, collected in new, clean 30 ml plastic bottles, specifically designed for the analysis of trace metals. These were filled to the top so as to avoid air bubbles and stored constantly under refrigeration at 4ºC. The first bottle was destined for the determination of anions and TOC, analysed on a Dionex Ion Chromatograph and a Shimadzu TOC analyser

respectively. The second one was acidified for conservation purposes using ultra-pure nitric acid (2%), down to a pH value of 1-2. This bottle was used to detect major cations as well as silver ion concentrations, performed with an ICP-OES and an ICP-MS, respectively (Table 3.3). Throughout the duration of the fieldwork process, these samples were stored at the SAPASMA lab under refrigeration. Upon completion of the sampling period, they were shipped to the UK in a Styrofoam cooler box using express courier services so as to minimize any variability due to changes in temperature. Arrival time was within a few days in both cases (2010 and 2012).

Cations and anions for the first round were analysed in October 2010 at the Wolfson Lab for Environmental Geochemistry at UCL. On this occasion a TOC analyser was not available, nor was the ICP-MS for silver analysis. These were added to the study for the second set, analysed as of November 2012. By then the EE lab based at the CEGE Dept. in UCL had purchased a new Ion Chromatograph, in which anion analyses were performed (Table 3.3).

For the sake of consistency and to minimise the possibility of errors, a labelling system for all field samples was devised, along with a standard sampling procedure (Annex B**)**, which was successfully implemented during both rounds.

Table 3.3. Parameters evaluated at UCL and methods of analyses

Parameter	**Equipment (2010)**	**Equipment (2012)**
Cations	Jobin Yvon Ultima 2 ICP-OES	Ibid.
Anions	Dionex 2000i IC [Wolfson lab]	Dionex ICS-1100 [EE lab]
Silver	NA	Varian 820-M ICP-MS
TOC	NA	Shimadzu TOC-L Analyser

3.2.4.4 Sampling points

The sampling points used for analysing the systems are described in Table 3.4. Point No. 3 was only implemented for the second round (2012). However, this sampling point was not available on each visit. The box where the filters and ioniser are housed could not be opened if the school happened to be closed (at times unpredictably) or the head-teachers were not present with the keys. Settling tanks were also empty on some occasions, due to cleaning for instance, and could not always be sampled. Wherever possible, duplicate samples were taken. Outlets were let to run for 1 minute (approx.) before collection.

Table 3.4. Sampling point description

ID	Point	Sampling notes
1	Settling tank	From plastic sedimentation tanks; corresponding to roof runoff
2	Cistern	In over-ground tanks sample was taken from a valve (5–10 cm above the bottom); in underground cisterns, it was taken from the suction of the pump, located roughly 20–30 cm over the bottom
3	Silver ioniser	From a sampling point located between the silver ioniser and the activated carbon/fine particle filters
4	Drinking tap	From drinking water fountains, usually let to run for at least 1 min before sampling to remove any stagnant water remaining on pipes

3.2.4.5 Data analysis

Given that it was not possible to take many repeated measurements at each site, as explained above, data obtained were considered to be qualitative rather than an accurate measurement of efficiency. ANOVA and t-tests were performed to evaluate removal rates using Microsoft Excel, applying log transformations for coliform counts. Covariance analysis and other tests were done using QI Macros, an add-on statistical package for Excel. Since all the systems were located in the same region, under similar conditions of rainfall and weather patterns, it was safely assumed for the sake of statistical analyses that all samples came roughly from the same source. Adding to the fact that quasi-identical treatment, filtering and storage materials were used on all sites, albeit with minor variations, the data set was combined to establish general trends of the system as a whole.

3.3 UCL LABORATORY EXPERIMENTS

The following sections describe the models, equipment and experimental setup used for laboratory work at UCL, which took place mainly from 2010 to 2012, interspersed with the fieldwork studies and other activities. It was decided early on to focus research efforts on silver ions, due to a number of constraints, setting aside other complementary fields (such as copper ionisation or silver nanotechnology) that had been considered at the onset of the investigation.

Experiments were divided into batch and continuous flow tests. The former were performed usually in beakers or other containers where silver ionisation, inoculation or other treatment was applied to a static water volume (Section 3.3.4 below). Continuous experiments, as the name implies, were those where the liquid was allowed to flow either by gravity or by pumping. Three continuous flow models were built for this purpose, one of them imitating as closely as possible the filtering and purification sequence used in the field. These models are described in Section 3.3.3.

Bacteriophage tests merit a section on their own, owing to their complexity, even though technically these would be considered batch experiments (3.3.5.3). Continuous runs using phages were not performed, due to the difficulties in making sure that there were no surviving particles after each assay, which could potentially affect future experiments by infecting any *E. coli* passing through. Furthermore, even though theoretically the viral strains used for this project are non-hazardous to humans, the possibility of mutations can never be discarded, and it was considered best to work only under strictly sterile conditions, using containers that could be either safely disposed of or autoclaved at the end of each run.

3.3.1 SILVER ION APPLICATION

3.3.1.1 Description of ionisation devices

Since the core innovation of the RWH systems under investigation is the silver ioniser, a brief description on its operating mechanism is warranted. Regardless of specific variations (discussed below), all units consist of two main components:

a) a pair of electrodes or cells, containing varying concentrations of silver
b) a DC power supply, which can be 'alternating' (i.e. switching polarities at fixed time intervals) or 'fixed', as in a conventional battery.

A positive DC voltage is applied to one of the electrodes, which then becomes an **anode**, releasing silver (or copper, depending on its composition) into the water. The positively-charged silver ions will be attracted to the negative electrode or cathode. However, natural convection and water flow (if existing) will allow for their dispersal. In addition, as more ions are released they will repel each other, forcing some of them to flow in opposite directions and eventually spread throughout the entire volume.

The idea behind an 'alternating' DC source (not to be confused with AC power supply) is that every few seconds or other fixed time period, the polarity will change, inverting the electrodes from anode to cathode and vice-versa. This would allow for an even wear of the silver cells. It is also meant to protect the negative terminal from becoming clogged with silver ions which may adhere to its surface, losing their charge and becoming pure metallic silver, a phenomenon known as 'plating out' in the electro-plating industry (Ammen 1986). This layer of uncharged particles will create a 'silver sludge', which will greatly reduce the efficiency of the electrolytic device by allowing less current to pass through. Some authors recommend using only one silver anode with a constant positive polarity, while using a neutral material such as stainless steel for the cathode (Stenulson 1998; Becker & Selden 1998).

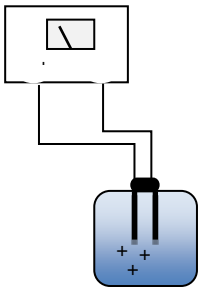

Figure 3.4: Diagram of silver ionising unit, showing charged ions

Silver Cells

With one exception (see below), all of the devices utilised for this research contain a pair of silver electrodes, made from minted 1-ounce[7] coins from the Bank of Mexico (defined as *Plata Ley 2009*) with a certified .999 purity. Three different units were used throughout the research project (all from the same supplier). For the sake of clarity, the code names assigned below will be used throughout this report:

Half-cell: This is a 'floating' device consisting of ½ coins (each electrode comes from a full silver coin cut in half). Cells are separated a distance of approx. 2 cm. They are attached to a PVC cap by a galvanized iron screws and water-proof sealed with an inert epoxy resin. Electricity is applied using the top of the screws. The cap with its two electrodes is in turn attached to a white Styrofoam sphere which will float in

[7] This refers to a troy ounce (the standard unit in the precious metal market), equivalent to 31.1g (approx.)

water, much in the manner of swimming pool floating chlorinators. The manufacturer's idea behind this was to create a unit that would spread ions more evenly over a large surface or water body (Figure 3.6 and Figure 3.7). This device was used in the lab solely for batch experiments.

A variation of this device was used in the field, using the same half-cells but connected to a 1.5" PVC cap[8], attached to the main water supply pipe by means of a 'T' junction, allowing for ionisation in line with the water flow (Figure 6.3).

Full-cell: This device is similar to the one above, except that full 1-ounce coins are used for electrodes, separated by a distance of 2 cm. The coins were originally attached to a 2" PVC (approx. 50 mm) screw cap. However, since standard pipe fittings in the UK vary to those in Mexico, a special set-up was made in the lab, removing the original PVC cap and attaching the electrodes (using the same screws) to a custom-made rubber lid (Figure 3.8). Using a standard Millipore 250 ml plastic filter-holder[9], an ionising vessel was created (Figure 3.5) with an input and output tube. Though this allowed for a greater retention time than the 'T' junction used in the field, the overall effect could be simulated while ensuring no leaks were present.

Ag/Cu: Even though copper ionisation is beyond the scope of the present work, a unit consisting of two silver/copper rectangular cells was obtained for the sake of comparison. Each electrode contains an alloy of 65% silver and 35% copper, according to manufacturer's specifications[10]. At present, there is a controversial EU ban on copper disinfection for drinking water, due to health concerns, although it can be safely applied to swimming pools and is commonly used to control algae and other microorganisms (Health and Safety Executive 2013). The device looks in every other respect identical to those described above. It was only used in the current research for limited tests. Table 3.5 summarises the main characteristics for each device used, including approximate volumes and surface areas.

[8] Standard US measurements (inches) are commonly used for plumbing in Mexico. Metric is preferred in Europe for pipes and fittings, creating important discrepancies as both fittings are usually not compatible.

[9] Millipore Catalogue No. XX1104705 (Polysulfone 250 mL filter receiver flask). When filled to the top, total measured volume was actually higher (approx. 300 ml).

[10] Personal communication (email) with Mr Federico Rodriguez (11/5/2011), manufacturer

Table 3.5. Summary of ionisation devices used for lab experiments

Device	**Description**	**Weight[1] unit** (g)	**Weight of cells**	**Dimensions** (cm)	**Area** (cm^2)	**[3]Volume** (cm^3)
Ag/Cu	Rectangular copper-silver electrodes	118.2	NA	2.4 x 1.6	3.8	1.2
Half-cell	Coins cut in half-moon shape, attached to a 'floating' unit	114.8	15.6 g (½ oz.)	[2]Diam.= 4.0 Width=2.0	3.1	0.9
Full-cell	Complete coins screwed to Millipore ionising vessel	175.2	31.1 g (1 oz.)	Diam.= 4.0	12.5	3.8

1. Weight of entire piece, including screws, etc. did not vary significantly after experiments (±0.1 g)
2. Only 2.5 cm of cell actually exposed, the rest is covered by epoxy sealant, not in contact with water
3. Thickness is 3 mm (approx.) for all devices. Distance between cells is also constant (2 cm)

Silver cells were regularly cleaned with a dilute acetic acid solution, particularly after experiments involving prolonged ionisation, in order to remove any discoloration.

Figure 3.5. Full-cell device with ionising vessel

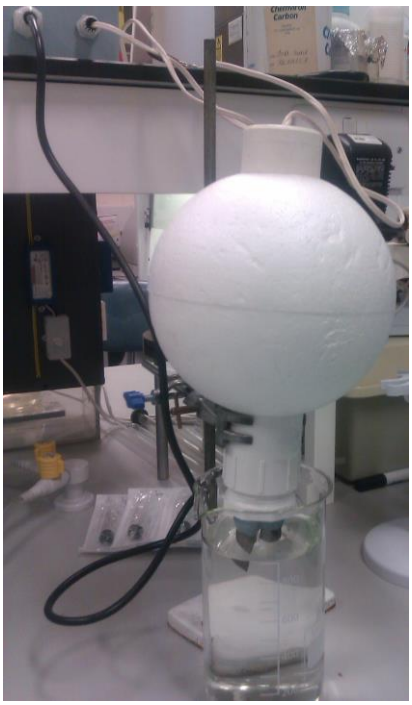

Figure 3.6. Floating silver half-cells

Figure 3.7. Half-cells submerged in water

Figure 3.8. Silver coins as electrodes (full-cell)

3.3.1.2 Other application methods

In addition to the units obtained in Mexico, a set of fine **silver wires** for extra testing was purchased from Cookson, a well-known precious metal distributor in the UK. The wires were fully annealed, at a purity of .99 (meaning at least 99% silver with the most likely contaminant being trace amounts of copper), and a 0.50 mm diameter[11]. This compares to the higher purity standard of the Mexican minted coins (.999). The wires were intertwined to make flexible 'silver rods' of the following dimensions:

Weight (g)	L (cm)	Thickness (mm)
2.3	35	1.0
2.0	30	1.0

In order to apply these silver rods for ionisation in water, a rigid plastic support was prepared (Figure 3.9) which could be suspended on top of a 1 L glass beaker (diameter = 10 cm). The rods were then passed through any of the small punched holes that were drilled at pre-set distances along the supporting bar. Clamp screws on the top side also allowed adjustment of the submersion depth (a variable named HSUB – see Annex A), as well as connection to the power supply, which was done via alligator clips (Figure 3.10).

Figure 3.9. Silver rods with supporting bar

[11] Cost was £0.94/g, not including VAT or shipping

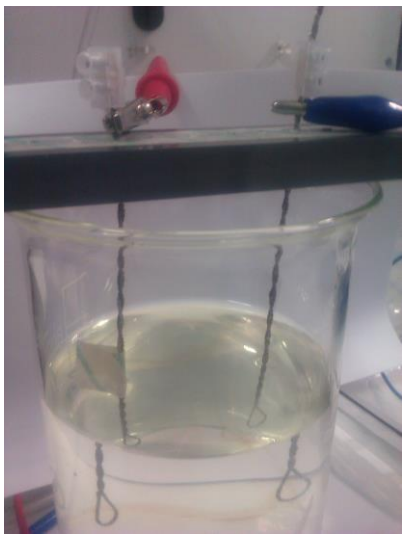

Figure 3.10: Energised silver rods in an experiment

For most experiments, the silver rods were submersed to an average depth of 5 cm. Distances (d) were varied to test changes in current and efficiency, ranging from 1 – 10 cm, limited by the beaker diameter. The rods were weighed before and after each experiment, with no noticeable change observed at the balance resolution used (0.1 g). Judging by the results obtained (5.1.3), these would be more likely in the order of µg and would require more precise weighing instruments.

Silver standards were also used for calibration and comparison, as well as for some microbiological tests. These were obtained from Hach and Jenway, both at a concentration of 1000 ppm, stored in a dark cupboard at room temperature while not in use. For the ICP-MS, special standards were used, also at an initial concentration of 1000 ppm.

3.3.1.3 Power supplies

The original system, utilised in the field and during the first lab tests, included a DC power supply, connected to the grid via an AC/DC transformer (designed for 110V AC). This was adapted to the UK 220V electricity using a standard transformer. An internal control circuit switches polarity on the electrodes approximately every 10 seconds. The applied DC voltage can be read by means of an analog meter on the display. Fuses are also installed in case of short-circuits on the electrodes or over-currents.

Both the silver cell assemblies and the switching power supply were manufactured by *SilverLife*, a Mexican company (www.silverlife.com.mx). In the later phase of lab tests, regulated 'fixed' power supplies were used, as well as standard 9V batteries, testing the effect of applying constant voltages on only one electrode in particular. In addition, a custom-built control unit was designed, using a state-of-the-art microprocessor, to switch the voltage polarities at user set times, allowing for greater functionality (Figure 3.12).

The question arises as to whether there is not a voltage drop between the screw terminals and the actual silver electrodes, given that they are made of different

materials. This was tested for all devices, using a variety of power supplies, and the voltages were shown to be the same all the way from the power supply to the tip of the coins (immersed in water). Thus, no significant electrical loss was observed across the system. An important exception to this was when a current meter was installed along the circuit, which can account for voltage drops of up to 0.5V, depending on the conductivity of the water being used (see 5.4). In general, every time a circuit contains a load and current is passing through it, there is a slight voltage loss. Standard electric nomenclature defines the open-circuit voltage (i.e. without any load) as **Voc**. Results reported in this thesis will usually be the regular operational voltage (V), except when specifically indicated otherwise.

Figure 3.11: Fixed power supply connected to continuous flow device

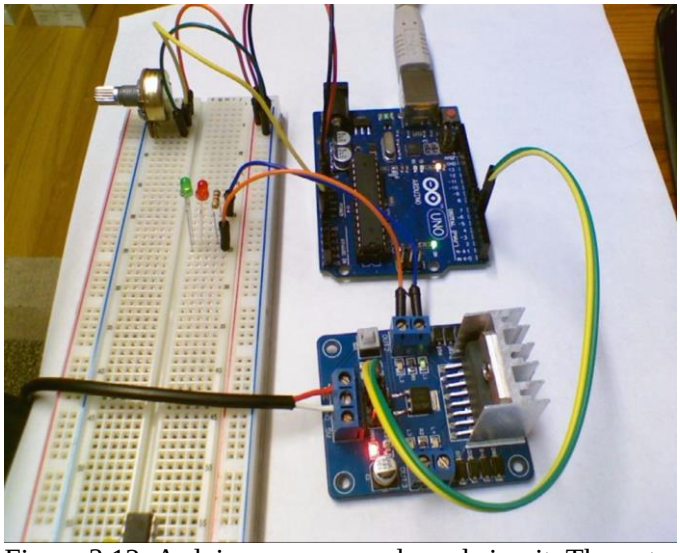

Figure 3.12: Arduino power supply and circuit. The potentiometer on the top left controls the switching time between alternating polarities

3.3.2 WATER SOURCES

Water used for experiments came from 3 different sources, chosen for their differences in conductivity and other physico-chemical characteristics:

a) Deionised water (DI) / Milli-Q: obtained from lab dispensers. Used for blanks and dilutions, as well as to represent the extreme case of little or no minerals, no interfering anions and very low conductivity.

b) Rainwater (RW): A 250 L rainwater barrel was installed outside the Environmental Engineering (EE) lab at UCL, collecting water directly from the rooftop. This water was stored without any exposure to light, and could be sampled as needed from a tap at the bottom of the tank.

c) Tap water: taken from taps around the lab, used to represent the other extreme of elevated mineral concentrations, interfering ions (such as chloride), as well as higher conductivity and hardness.

The idea behind using various water supplies was to compare the behaviour of the ionising devices in different media, with the aim of better understanding the mechanisms involved. Since ionisation in water is highly responsive to conductivity, it was considered important to provide a reasonable range of operation, without adding chemicals which could potentially interfere with the process. Combined, the 3 sources described form a conductivity 'spectrum', with rainwater somewhere in between, as can be judged from Table 3.6. Measurements were taken at random intervals throughout the entire duration of the research project.

Table 3.6. Conductivity and pH values of test water sources

Water type	**Conductivity** (µS/cm)[1]	**pH**
DI	3.1 (0.8)	5.72 (0.17)
RW	68.1 (6.8)	6.78 (0.11)
Tap	692.8 (21.4)	8.03 (0.04)

1. Standard error of the mean (SEM) in parenthesis, rounded to nearest decimal (N=7)

Room temperature inside the lab was measured to be relatively stable around 24°C, roughly equivalent to water temperature at the time of sampling. However, rainwater in the external tank varied according to seasons, with a measured range of 1 – 25 °C. To compensate for any possible errors resulting from this, samples were always left to sit at room temperature in the lab for a few hours before analysing.

3.3.2.1 Rainwater characterisation

RW conductivity values at the water butt ranged from 50 – 90 µS/cm, but tended to increase slightly upon interaction with the holding tanks, pipelines and filters. TOC and IC (Ion Chromatography) analyses are shown in Tables 3.7 – 3.9.

As expected, TOC values were found to be low, with a mean (from the measurements above) of 4.0 mg/l. Inorganic carbon (IC) accounted for over half of the Total Carbon (TC) content in some measurements. BOD was measured once (17/1/11); found to be 4.46 mg/l. Dissolved Oxygen (DO) was measured on 30/1/12, finding a relatively high concentration (8.9 mg/l; 94% saturation). A set of measurements taken over the summer of 2011 revealed an average of 6.8 mg/l DO in the same rainwater butt (Daglis-Pagotto 2011)[12]. These could have been due to recent rainfall events, since stagnant water in a closed barrel would tend to have a gradual oxygen drop. However, rain gages or other weather monitoring devices were not used during the project, so this value could not be properly correlated to precipitation, a factor considered secondary to the main research aims of the present study.

Table 3.7. TOC values (in mg/l) of RW from rainwater butt

Sampling Date	TOC	Inorganic Carbon (IC)	Total Carbon (TC)
17/01/11	2.43	2.74	5.17
23/11/11	4.50	6.41	10.91
31/01/12	5.51	9.36	14.87
06/03/12	3.64	3.51	7.16

Table 3.8. Measurement of anions in rainwater butt (mg/l)

Sampling Date	Cl	NO_3	SO_4
21/7/11	2.05	4.97	3.83
25/7/11	1.01	4.14	ND
22/9/11	2.98	10.08	14.81
31/1/12	4.77	12.06	7.86

ND: Not detected (i.e. below detection limit)

[12] Standard deviation (SD) was 0.36 mg/l (n=5)

Table 3.9. Main cations in external rainwater butt (mg/l)[1]

Sampling Date	Na	K	Ca	Mg	NH_4
01/12/12	7.80	0.56	2.77	0.43	ND
02/12/12	3.05	0.39	7.05	0.35	0.38
28/11/12	2.14	0.51	7.68	0.34	ND
28/11/12 [2]	2.95	0.48	8.87	0.42	ND

1. Silver was measured and not detected in any of the samples

2. Sample taken after transferring from RW butt to holding tank in the lab (Figure 3.13)

Microbiological analyses were done for the presence of *E. coli* and naturally occurring bacteriophages, but none were found in any concentration. Total coliforms were observed in relatively low quantities in 2010 and 2011, with samples roughly a year apart, finding between 10 and 100 CFU/100 ml. A study from the same rainwater butt performed by an MSc student (Daglis-Pagotto 2011) found low concentrations of *E. coli* in only 2 out of 6 samples (8.8 CFU/100 mL mean value), and a total coliform average of 32.5 CFU/100 ml. Incidentally, the same study found an average conductivity of 58 µS/cm (n=5, SD=0.015), and a pH mean value of 6.7 (n=7, SD=0.15) confirming the results obtained above.

3.3.3 CONTINUOUS FLOW

3.3.3.1 Model I: Ionisation and filtering

This model emulated the systems set up in the field, being the only one requiring a pump to operate. It consists of the following main components (Figure 3.13):

- Two plastic containers (approx. 20 L each) connected to a pump, where with valves either tank can be selected to pass water through filters. In this manner, two different influents could be stored (i.e. with or without silver ions). The height difference between the pump and the prefilter is 1.2 m, connected by a 22 mm copper pipe.
- 100 µm stainless steel prefilter, purchased through a UK supplier, with a manual backwash mechanism, similar to those used in Mexico (although different brands).
- 2-stage filter, purchased locally, similar to the ones used in the field (20" housing). The first cartridge is made of disposable polypropylene spun fibre, to capture fine solids, and the second one contains GAC and KDF, in roughly an 80-20 proportion.
- Sampling valves inserted at different stages along the purification line, allowing for silver concentrations and other parameters to be monitored in a continuous flow operation.

Several litres of fresh RW were flushed in between tests to ensure that no carry-over of ions took place from one run to the other. This model was not used for microbiological tests. These were reserved for batch experiments and for Model III (see below), where the components could be safely autoclaved after each run.

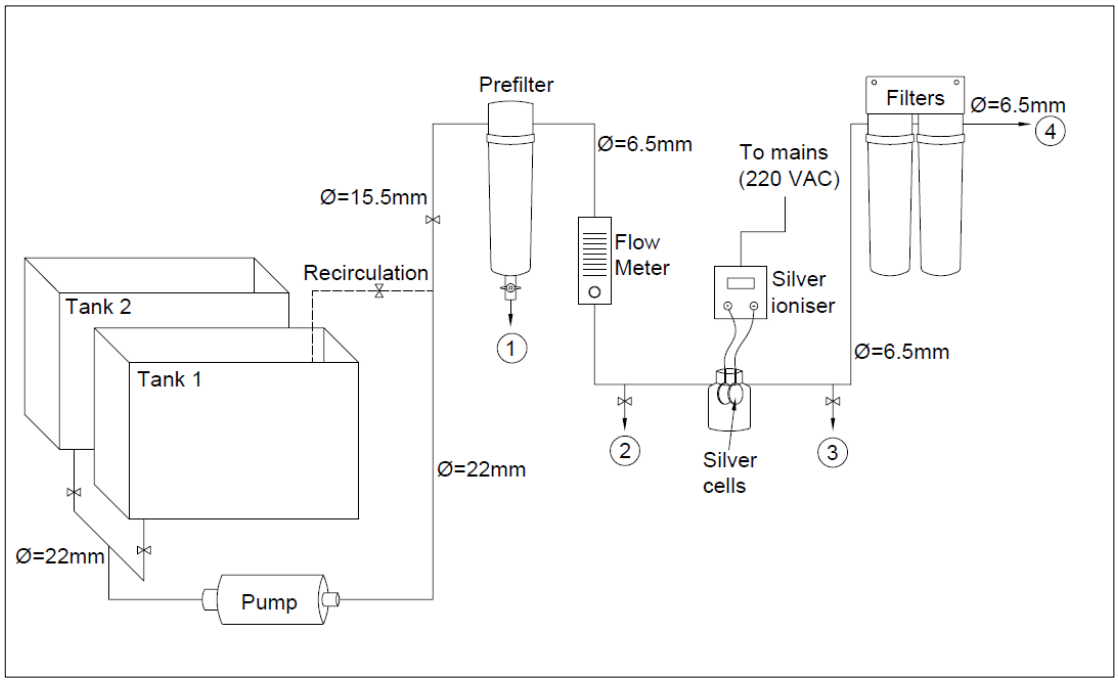

Figure 3.13: AUTOCAD rendition of Model I showing sampling points

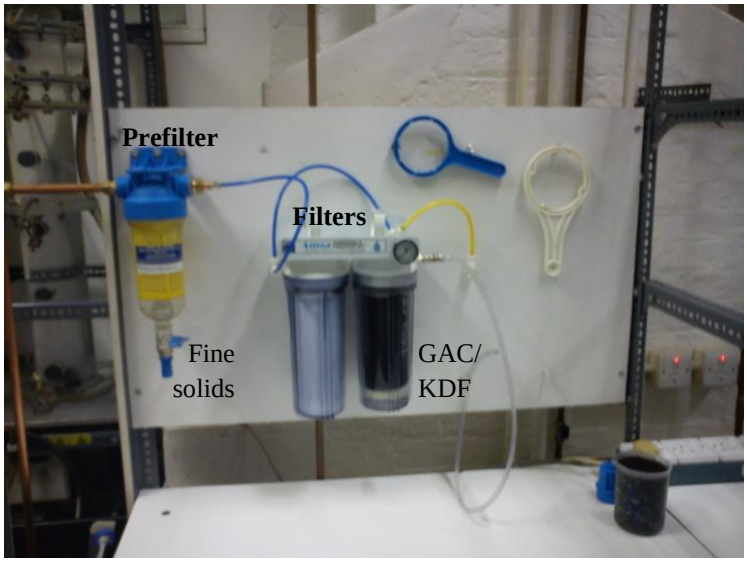

Figure 3.14: Model I setup with stainless steel pre-filter (left) and 2-stage filtering unit (silver ioniser not shown)

3.3.3.2 Model II: Tubular flow

This model, operated strictly by gravity, was set up to examine the dispersion of ions through a pipe, without the filtration components. It was also used to test for a possible correlation between turbidity and electrolytically generated silver (i.e. not

from silver standards) which was discovered early on, and could potentially provide a simple and cost-effective means of determining if the system is operating properly.

Both RW and Tap water were used and compared: These were fed into the beaker shown on the left of Figure 3.15. Several litres of the selected water source were passed through the model before each experiment, to flush out any traces of silver or other elements from previous runs, and to ensure that no air bubbles were trapped along the ioniser vessel or on the tubes. As a general rule, enough test water was flushed to ensure that both turbidity and conductivity at the input and output (points 1 and 4) were homogenised (within 5% difference).

RW was pre-filtered before addition to the model. This was done by passing it through a 100 µm stainless steel filter (Figure 3.14), which will take out large particles that might otherwise disrupt the experiment, without changing any of its basic characteristics.

Although this is classified as a continuous flow system, its main objective was to investigate ion 'spread' or diffusion under mainly static conditions. The only flow that occurred was when water was actually drawn out for sampling. The long pipe in the centre is made of transparent acrylic (inner diameter = 43 cm), allowing for visual inspection, and contains two intermediate sampling points (shown as 2 and 3 in the figure). The flexible rubber hoses interconnecting the components have a ⅜" (≈1 cm) diameter. The ionising vessel is the same one used for other continuous flow experiments (full-cell device), with an estimated 300 ml volume (Table 3.5). The total holding capacity of the model when filled with water is 1.2 L, approx. This model was not utilised for any microbiological tests, as disinfecting and autoclaving the components would have been challenging.

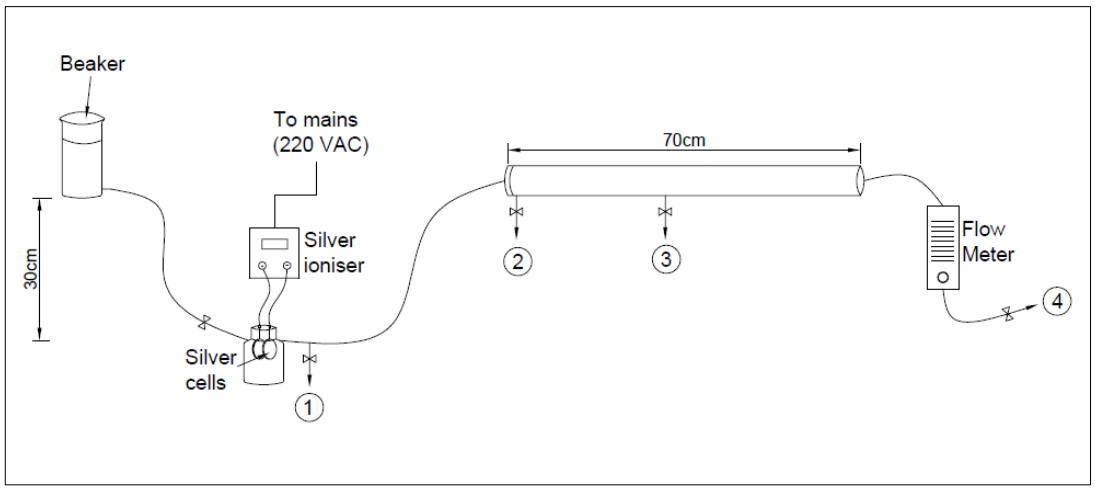

Figure 3.15: AUTOCAD drawing of Model II (gravity-fed tubular flow)

3.3.3.3 Model III: Gravity flow

This setup is a simplified version of Model II. It was basically used for microbiological tests, since the components could be disassembled and autoclaved

after an experiment, and for continuous RW runs with low flow rates (Figure 3.16). Flow was regulated by opening the valve in sampling point 2, and kept constant by manually adding water to the glass beaker at regular intervals, which acted as a 'feeder tank' to the system.

Between experimental runs, several litres of pre-filtered RW were passed through, in order to thoroughly flush the system from any remaining ions. Inoculation was performed by adding a stock of bacteria to the elevated beaker. For this particular model, only the fixed power supply was used (3.3.1.3). The polarities were manually inverted between runs to avoid an uneven wear on any one of the electrodes. Silver was analysed in the lab using the Hach spectrophotometer.

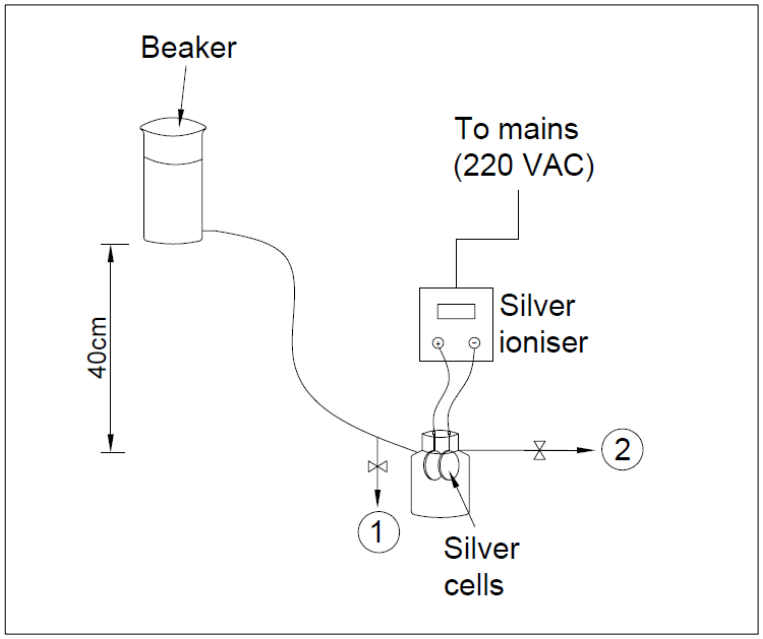

Figure 3.16: Schematic of Model III (gravity flow)

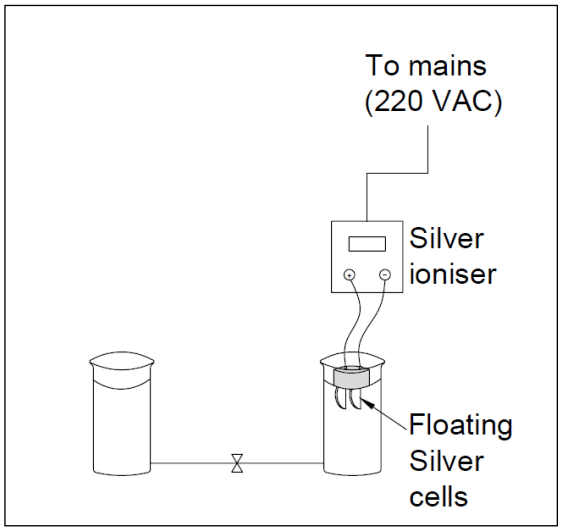

Figure 3.17: Diagram of Ion Diffusion experiment

3.3.4 BATCH EXPERIMENTS

3.3.4.1 Ion diffusion (lab set-up)

Experiments to examine the diffusion of silver ions over time, in different configurations and test waters, were set up in the lab, with the main one shown in Figure 3.17.

Two interconnecting glass beakers, each with a 600 mL capacity, were joined via a 52 cm flexible rubber hose (external diameter=8 mm, internal≈5 mm), with a valve in the middle for regulating the flow between them. The half-cell 'floating' device (3.3.1.1) was used in the first beaker to generate silver ions. Silver concentrations were tested and compared in both beakers. The valve was maintained closed while sampling and opened during ionisation. Different water types with varying conductivities were used in this experiment for comparison. To maintain standard testing conditions as much as possible, water volume on both beakers was kept at approximately 400 ml for all test runs.

A **vertical glass column** with the following dimensions was also used for examining the up-flow diffusion of ions:

Height = 31.5 cm (water level)
Diameter = 5.5 cm

In this case, a previously prepared silver solution of known concentration was poured to the bottom of the column, with raw RW carefully added above. Samples were taken from the top without any form of stirring, at a measured time interval, allowing for a general determination of up-flow silver ion diffusion.

Other ion diffusion experiments were performed using lab Model II (tubular flow), described in the corresponding results section (5.2.2).

3.3.5 LAB METHODOLOGY

3.3.5.1 Measuring equipment

Table 3.10 shows the main equipment and methods used for the various laboratory tests. Some equipment was found to not be applicable to the project. For instance, the ISE (Ion Selective Electrode) probe was observed to be, after thorough testing and despite manufacturer's claims, non-linear, unstable and inaccurate for the low range readings required (<1 ppm Ag). It was thus discarded as a valid method for silver testing. The model used is still included in Table 3.10 for the sake of reference.

Other equipment and procedures became only available at a later stage, or were used only sporadically due to high cost. Silver was measured for the most part using a portable Hach spectrophotometer; a method which was found reliable and relatively fast for the ranges required (requiring 4-5 minutes per test). Occasionally, for lower ranges and more precise measurements, as well as for preserved samples collected in the field, an ICP-MS was utilised. Due to high operative cost and availability, it could not be used continuously for all experiments. Samples for analysis by ICP-MS were acidified using Optima ultra-pure nitric acid (2%), down to a pH value of 1-2, to avoid the formation of silver chlorides.

Deionised and ultra-pure Milli-Q water for all experiments were provided in the laboratory by *Purite Select* dispensers. Bacteria (i.e. total coliforms and *E. coli*) were tested using the membrane filtration method and m-Coliblue® 24 broth, the same method used in fieldwork, in order to achieve consistent and easily comparable results. This procedure is approved by the USEPA and provides a direct method to read both total coliforms and *E. coli* in one test, within 24 hours (Crane et al. 2006). All microbiological samples were collected in sterilised containers.

As shown on Table 3.10, conductivity was measured using three different techniques. The ECTestr meter, which was also used during fieldwork, has the advantage of portability and was utilised in some lab tests, but offers limited accuracy as measurements jump in intervals of 10 µS/cm. The more precise Mettler-Toledo meter was available at a later stage of the research. It was compared to the meter used until then (Jenway 4330) with very small variations[13]. Where a specific equipment or method was used for a test, it is mentioned in the corresponding results section (Chapters 4 and 5).

[13] In a RW sample 180.0 µS/cm was obtained with the Jenway meter and 180.8 with the Mettler-Toledo

Table 3.10. Summary of equipment used for UCL lab research

Parameter	**Equipment / Method**
Cations/Anions	Dionex ICS-1100 [using Cation or Anion column]
Silver	Varian 820-M ICP-MS
	Hach DR2800 Spectrophotometer
	Jenway Silver Combination ISE S/N 1065
TOC	Shimadzu TOC-L Analyser
Conductivity, pH, TDS, Temperature	Jenway 4330 Conductivity & pH meter
	ECTestr Conductivity meter: low (0– 1900µS)
	Mettler-Toledo *SevenMulti* Meter
Electric parameters	UNI-T Multimeter, Model UT30B [R, I, VDC]
Total coliforms, *E. coli*	Millipore m-ColiBlue24® Broth (Membrane Filtration method)
Bacterial counts (general)	Miles & Misra Method[14], plated on Tryptic Soy (TSA) or Nutrient Agar (NA), according to test.
Bacteriophages	Tested according to BS EN ISO10705-2 (2001)
Oxygen (DO)	Jenway 9200 DO Meter
Turbidity	Hach Ratio/XR Turbidimeter (0-2000 NTU)
	Hach 2100AN Turbidimeter (ISO 7027 method)
Weight	Oertling F22T0 Scale

[14] The Miles & Misrah method for determination of total bacterial counts is described in Miles et al. (1938).

3.3.5.2 Inoculation

Some experiments involved inoculating water with high counts of microorganisms to check for efficiency or survival rate under specified conditions. Initially, the K-12 strain of *E. coli* was used for this purpose, as it was readily available at the lab. This stock was originally purchased from LGC Standards in the UK (ATCC 25404). However, once bacteriophage testing was introduced (see section 3.3.5.3 below), another variety of *E. coli* known as WG-5 was utilized, as it had to be used for phage testing anyway. This particular strain is resistant to some antibiotics, such as Nalidixic Acid, and was thus considered to be a good indicator for disinfection-related tests. The original stock was obtained from the University of Brighton (School of Environment & Technology).

Bacteria were stored in 2 ml vials, refrigerated inside cryogenic boxes in a -80°C refrigerator. PBS (Phosphate Buffered Saline solution) was used for dilutions and for conserving the stocks of bacteria (with 10% glycerol added as an anti-freeze). Occasionally, bacterial counts in random vials of a given stock were performed by using the Miles & Misrah method (Miles et al. 1938), to determine their readiness for experiments.[15] If the stock was not found viable or containing counts which were lower than expected, it was discarded. Experimental inoculation was performed in two different manners:

a) Direct addition, where a vial was warmed to room temperature and added directly, without dilution, to a volume of test liquid (such as rainwater).

b) Pre-growth, adding the bacteria to a broth, with constant stirring and incubating at approx. 36°C for a few hours, or till a high enough optical density was achieved, and then adding a fixed amount to a volume of test liquid, depending on the desired final concentration.

In most cases, the inoculated liquid was stirred to guarantee a homogenous distribution.

3.3.5.3 Bacteriophage testing

The author undertook training on an emerging technique for the determination of viral phages in water during the summer of 2011, at the University of Brighton, under the

[15] *E. coli* vials were usually found to be in the range of 10^8 CFU/ml

guidance of Prof Huw Taylor and Dr James Ebdon. Methods for monitoring both anaerobic *Bacteroides*-infecting coliphages and general somatic coliphages (associated with *E. coli*) were covered. However, only the later was added as a further research component, since the former (*Bacteroides*) inhabit mostly anaerobic environments and are linked to human faecal contamination, associated largely with wastewater or sewage, a condition that is clearly not applicable to the present research. Somatic coliphages, on the other hand, represent a general indicator of faecal pollution stemming from other animals which can be found on rooftops, such as birds or rodents, and can survive under aerobic conditions, making their presence in rainwater tanks more viable (Ibarluzea et al. 2007).

Testing and analyses were performed in accordance with BS EN ISO10705-2 (2001), by growing a WG-5 *E. coli* host on MSA agar plates and counting the 'holes' in the agar (where viral particles infected the bacteria) after 20-24 hour incubation at 36°C. Stock phages for inoculation experiments were obtained from natural water samples (i.e. River Thames). Using sterile technique, viruses were scraped from the agar plates after culturing and diluted in a special phage buffer (Table 3.11), empirically tested with good results (Kutter & Sulakvelidze 2005). Using this method, several titres were prepared at varying concentrations (with approximately 10^6 pfu/ml the highest) and stored in a 4°C refrigerator while they were being regularly used. Subsequent tests showed that the numbers did not drop significantly even after several months of storage at this temperature, and thus freezing was not required.

Table 3.11. Phage buffer ingredients

Substance	Concentration (mM)
Na_2HPO_4	19.519.5
KH_2PO_4	22.0
NaCl	85.5
$MgSO_4$	1.0
$CaCl_2$	0.1

Inoculation was done in a similar way as for bacteria, by pipetting the required dilution (according to the concentration desired) into a larger volume of test water. Continuous stirring was usually done throughout experiments to guarantee a uniform distribution.

Due to health and safety concerns in the lab, bacteriophages were not run through any of continuous flow lab models discussed here, but strictly in batch experiments where all of the components could be duly sterilised. The ionisation devices could not be used for the same reason, as any surviving particles (for instance, clinging to the rubber or adhesive sealant of the silver cells) could easily infect other microorganisms and disrupt the potential for further experiments. Furthermore, even though somatic

coliphages are not considered to be pathogenic to human beings (Kutter & Sulakvelidze 2005), virus are known to have the ability of mutating rapidly, which always poses a threat, particularly when working in a lab that is not specifically suited to a high level of microbiological safety. In consequence, silver addition was performed using previously prepared dilutions at the desired concentrations.

3.3.5.4 Data Analysis

Statistical analysis for the lab work was done using SPSS software, version 21 for Windows. ANOVA and t-tests were performed for most comparisons. Pearson's correlation coefficient (r) was utilised for correlation, with $r > 0.5$ considered a 'large' effect (Cohen 1992). Linear regression was also used for silver ionisation. Confidence intervals of 0.95 were generally used. Due to its widespread use in the literature, the p-value approach was employed to report significance (Montgomery 2012; Edwards 1980). For a definition of the variables used in SPSS, see Annex A.

3.3.6 LAB WORK SUMMARY

The following table summarises the lab models and devices used, including the main control variables as well as other parameters measured. Anions and cations were also measured occasionally, but were not analysed repeatedly enough or with the degree of precision required to be considered critical variables to this research (this was mainly due to calibration limitations of the IC instrument for low concentrations).

Table 3.12. Summary of experiments

Experimental Setup	Device[1]	Water sources	Main Variables[2]	Secondary variables
Model I	Full-cell	RW	V, Q, Ag, Cond, (ionisation) time	pH, I, cell angle, power supply, TDS
Model II	Full-cell	RW, Tap	Turbidity, V, Q, Ag, Cond, time	pH, I, cell angle, TDS
Model III	Full-cell	RW	Coliforms, V, Q, Ag, Cond, time	pH, I, cell angle, TOC
Batch	Half-cell, rods, silver standards, Ag/Cu	DI, RW, Tap	Bacteriophages, Coliforms, Ag, V, time, Vol, Cond.	Container type, pH, I, TDS, TOC, power supply, HSUB, Dist.

1. Variables are fully defined in Annex A
2. For a description of devices see Table 3.5

4 FIELDWORK RESULTS

This chapter contains the main results obtained in the field throughout both sampling periods, as described in the methodology (3.2). The two data sets are presented in chronological order, with a summary and discussion at the end of each section.

4.1 FIRST DATA SET - 2010

4.1.1 INTRODUCTION

Sampling took place between April and June of 2010, after unexpected torrential rainfalls during February 2010, which caused flooding throughout the region. Precipitation for this month alone according to local weather data reached a record 167 mm, as compared to 0 mm in the previous year (Green Map 2012). Paradoxically, the country overall experienced lower rainfall than normal (CONAGUA 2012). The concentrated heavy rains filled the cisterns. Since this occurred in the midst of a dry season, tanks were empty or nearly empty beforehand. It is possible then to assume that most of the water sampled came from this period, having been in storage for approximately 2 months.

As described in section 3.2, a selection was made out of the original systems as to which were the most suited for the study. From a total of eleven functional sites, nine were found to be viable for sampling and research during this particular period, the remaining two being unavailable due to maintenance. Site numbers in the text below refer to those in Table 3.1.

4.1.2 FIELD MEASUREMENTS

Table 4.1 summarizes the main results obtained from field data for the nine sites, evaluated along each point of the treatment system. As shown in Figure 4.1 COD drops significantly ($p=0.0026$)[16] with the first flush/ settling tank alone (77% reduction). A further 41% removal is achieved by the filtering treatment system, possibly aided by additional sedimentation occurring in the cistern itself. Evans et al. (2009) have also suggested the possibility of a beneficial micro-ecology in rainwater cisterns, whereby a host of bacteria may accelerate the degradation of organic matter and improve water quality, although this has not been verified in the present study.

[16] Using a two sample t-test (assuming equal variances)

Table 4.1. Summary of basic sampling parameters. Values for standard error of the mean (SEM) shown in parenthesis next to averages (n=9)[1]

	Settling Tank		Cistern		Drinking Tap	
Parameter	Range[2]	Mean	Range	Mean	Range	Mean
Temp (°C)	16.6 - 28.5	21.2 (2.1)	16.1 – 24	21.4 (0.9)	16 - 35	22.8 (2.0)
pH	6 - 6.7	6.4 (0.1)	6 - 7.3	6.6 (0.2)	6.3 - 7.1	6.8 (0.1)
Conductivity (µS/cm)	80 – 170	108 (15.9)	40 – 150	83.3 (18.9)	60 - 150	110 (17.3)
COD (mg/l)	10 – 76	47.9 (7.8)	3 – 25	11 (3.5)	2 - 18	6.4 (2.4)
DO (mg/l)	2.6 - 4.1	3.5 (0.3)	2.8 - 4.7	3.8 (0.3)	1.9 - 3.7	2.8 (0.4)
Hardness (mg/l)	25 – 200	65.7 (22.9)	10 – 250	80.6 (28.2)	25 - 200	67.8 (19.0)
Alkalinity (mg/l)	40 – 180	65.7 (19.9)	10 – 240	77.8 (26.9)	20 - 240	73.3 (23.1)

1. Due to a number of limitations, it was not always possible to measure all parameters for each sampling point. This is reflected in the SEM calculations which are adjusted accordingly (n<9)
2. Range refers to minimum and maximum values for all samples collected

Silver was found to be consistently lower than 5 ppb, which is the detection limit of the instrument used (Table 3.2) for the samples evaluated. Readings were usually 1-2 ppb at the Drinking Tap point, but cannot be relied upon given this detection limit. An ICP-MS was not available at this stage, as previously described.

DO levels remained relatively low throughout the system (Figure 4.1), which is a likely consequence of the water being stored for a few months without much movement or aeration. It is noteworthy however that the settling tanks with considerably more organic matter and visual contamination do not have lower DO levels. This may be due to the fact that settling tanks are cleaned and emptied more regularly than cisterns, which can potentially store rainwater for an entire year.

Finally, pH was observed to remain at slightly acidic to neutral values. From the first point (settling tank) to the final point of use, conductivity also remained constant, with a significant drop in the cistern, possibly due to the greater dilution of total dissolved solids and their subsequent concentration in the filters and narrow pipes. Conductivity, hardness and bicarbonate alkalinity are considerably lower than in municipal well water (ESF 2006), as would be expected from rainwater, while displaying no significant variation throughout the treatment system.

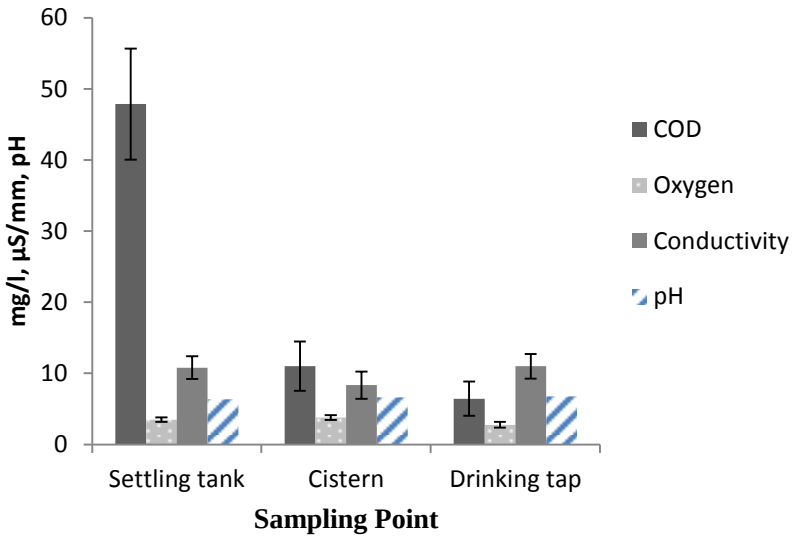

Figure 4.1: Comparison of selected field parameter means. SEM values shown in black line (except for pH, where variation is too small to be represented). Conductivity is shown in µS/mm for the sake of comparison.

4.1.3 MICROBIOLOGY

Only total coliform counts were read during this fieldwork round, since *E. coli* was not reported in any sample. This could, however, be due to an omission rather than a verifiable fact, since results in the 2012 sampling round did show faecal coliforms in some of the cisterns. Notwithstanding, disinfection efficiency can be safely construed from total coliform counts, since their absence naturally implies an absence of all other sub-groups (such as *E. coli*).

Three samples were taken for each site, corresponding to the treatment stages described above (settling tank, cistern, drinking tap). The only exception to this were the settling tanks where only 7 could be sampled, since those at sites #4 and #8 were empty, presumably for cleaning. Where higher counts were expected, a 1:10 dilution was done on the samples as they arrived into the lab. Due to budgetary constraints no duplicates were taken.

Sites #1, #3 and #4 showed zero coliforms on all samples, including in the settling tanks, suggesting a clean runoff not requiring disinfection or further treatment. Mexican drinking water quality guidelines require an absence of faecal coliforms, allowing up to 2 CFU/100 ml for total coliform counts (Secretaría de Salud 1994). Table 4.2 shows measured values for the rest of the sites, including efficiency of the settling tank and of the filtering/ silver ion system. With the exception of site #9, all the systems showed a highly efficient disinfection rate, down to levels deemed acceptable by WHO standards, which suggest a more ‘lax’ (and thus realistic) target for rural water supply in developing countries (WHO 1997).

Site #9 displayed an inordinately high bacterial load in the settling tank, which was not eliminated throughout the treatment process. Since only one dilution was

performed, and colony counts over 200 in the filter (according to the method) are very difficult to read, it is estimated that TNC refers to at least 2000 CFU/100 ml. Coliform presence in the cistern and at the final tap were probably lower, judging by the lower COD (Table 4.1) and better visual aspect of the water, yet were still too numerous to count without further dilutions, in sharp contrast to all the other sites. At the actual site, a large fissure was observed on the lid of the geomembrane cistern which allowed debris and decaying organic matter to seep into the tank. The result at the drinking tap, however, is surprising, since the silver ioniser was observed to be working at a normal voltage of 5V. Residual silver, on the other hand, was measured to be very low (only 1 ppb), leading to a possible recontamination of the liquid in the pipes, which in this case were partially exposed to the sun[17]. Due to the poor water quality of the cistern, the school teachers had decided not to drink the water till the lid was repaired, confirming that the filtered rainwater was stagnant in the tubes for a long period of time. Another possibility is that an error could have occurred during the analysis itself. Unfortunately, it was not possible to re-test the original sample, as after 24 h these are no longer viable for bacterial analysis. An attempt was made to return to the site for obtaining a confirmation sample, but access was blocked due to heavy flooding along the way (for a discussion on the limitations of fieldwork in general, see 6.3.2).

Site #6 also displayed a high number of coliforms in the initial stage, possibly due to a birds' nest found right on the downspout of the main gutter and overhanging trees on top of the roof. Nevertheless, coliforms were still substantially decreased by the settling tank alone (98%), showing a thorough elimination down to drinking water standards after the purification system (Secretaría de Salud 1994). Figure 4.2 displays comparative bacterial reductions within selected sites using logarithmic values.

[17] Ambient temperature was 30°C at the moment of sampling (1/6/2010)

Table 4.2. Total coliform counts for selected sites (CFU/100 ml)

Site No.	2	5	6	7	8	9
Settling Tank (ST)	550	8	1650	119	NA	TNC
Cistern (CIST)	6	3	26	17	3	TNC
Drinking tap (DT)	4	3	2	0	0	TNC
Removal due to settling[1]	98.9%	62.5%	98.4%	85.7%		
Removal due to treatment[2]	33.3%	0.0%	92.3%	100%	100%	
Total Removal	**99.3%**	**62.5%**	**99.9%**	**100%**	**100%**	

1. Total coliform removal (%) between settling tank and cistern (i.e. due to settling/first flush action)
2. Total coliform removal (%) between cistern and drinking tap (i.e. due to filtering/silver ion system)

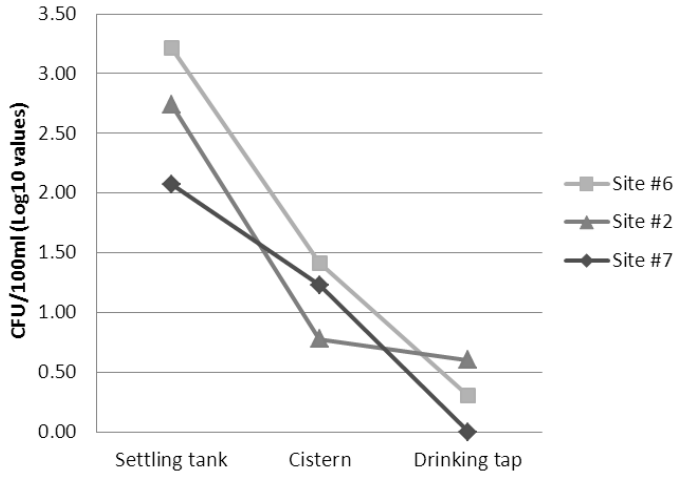

Figure 4.2. Total coliform removal efficiency for selected sites, in logarithmic values

4.1.4 LAB ANALYSIS OF FIELD DATA (UCL)

As described in the methodology on Chapter III, two additional samples (anions and cations) were taken in selected sites and shipped back to UCL for further analyses. Deep wells which supply drinking water to some communities were also sampled, particularly those where high fluoride concentrations were suspected. This was to corroborate and get additional data on one of the main motivators behind the systems

(poor groundwater quality)[18]. Analyses took place at the Wolfson Laboratory in London, on October 2010.

4.1.4.1 Rain samples

Table 4.3 summarizes results obtained by ICP-OES for cations and Ion Chromatograph (IC) for anions. In general terms, concentrations of Ca, K, Mg, Na, F, Cl, NO_3 and SO_4 decline in passing from the settling tank to cistern to drinking tap, with the most significant decline from the settling tank to the cistern. These declines are likely due to either dilution or the precipitation of secondary minerals such as carbonates, which would have co-precipitated the elements. The consistency in these patterns is different to that observed by Morrow et al. (2010), who documented higher degrees of element variability at different points in rainwater harvesting systems in Australia.

Table 4.3. Cation and anion compositions in mg/l (SEM values shown in parenthesis)*

	Settling Tank		**Cistern**		**Drinking Tap**	
Cations	Range (mean)	N	Range (mean)	N	Range (mean)	N
Ca	4.17 - 12.44 (9.75)	4	0.85 - 16.45 (7.58)	5	4.82 - 16.01 (9.93)	5
K	0.62 - 9.38 (3.21)	4	0.72 - 3.32 (1.52)	5	0.87 - 1.99 (1.42)	5
Mg	0.13 - 0.51 (0.31)	4	0.11 - 0.82 (0.36)	3	0.05 - 0.63 (0.36)	4
Na	0.34 - 19.37 (5.26)	4	0.19 - 9.44 (3.23)	5	0.51 - 10.73 (5.17)	5
P	0.03 - 0.16 (0.08)	4	0.02 - 0.06 (0.04)	3	0.010 - 0.014 (0.012)	2
Anions						
F	0.18 - 0.25 (0.22)	4	0.07 - 0.54 (0.23)	5	0.09 - 0.58 (0.27)	5
Cl	1.34 - 4.01 (2.52)	4	0.63 - 2.52 (1.48)	5	0.45 - 6.17 (2.26)	5
NO_3	2.42 - 9.15 (5.58)	4	1.42 - 8.59 (3.84)	5	0.1 - 9.26 (3.7)	5
SO_4	5.68 – 13.6 (9.58)	4	2.04 - 9.77 (4.51)	5	3.07 - 10.24 (6.16)	5

*N refers to number of samples where a reading higher than the minimum detection value was obtained

[18] This was offered to SAPASMA and to the Ecology Dept. in exchange for the generous offer of the local lab and logistical support.

4.1.4.2 Well water samples

As a complement to the fieldwork research, samples were also collected from selected drinking water wells in the municipality where the RWH projects were installed. The readings for anions and cations obtained are shown in Table 4.4. Results are in agreement with other studies on well waters in the region, performed mostly to detect high fluoride levels (ESF 2006).

Arsenic was evaluated in random samples, with all readings below the detection limit. Although a detailed groundwater analysis is beyond the scope of the present research project it can be noted that fluoride is present in considerably high concentrations in almost all samples. Cells shaded in grey on the table reflect values higher than the 1.5 mg/l guideline allowed at present by local and international standards (Secretaria de Salud 1994; WHO 2008). This corroborates the necessity of cost-effective alternatives for drinking water in the region, such as RWH.

Table 4.4. Chemical characteristics of well water samples in mg/l (June, 2010)

Community	**Ca**	**K**	**Mg**	**Na**	**F**	**Cl**	**NO_3**	**SO_4**
Don Juan	72.58	13.87	4.62	47.60	3.52	2.65	13.88	29.59
La Aurora	45.92	12.34	1.23	37.15	5.51	7.66	ND	6.73
Montecillo de Nieto	33.10	5.71	0.33	64.47	3.86	13.29	11.78	32.16
Atotonilco	40.57	9.17	1.57	90.57	2.64	29.56	33.73	83.44
La Cieneguita	22.05	4.75	0.14	65.80	2.03	7.90	4.96	18.85
Aug. Gonzalez	31.37	9.64	2.89	48.16	5.21	2.83	6.12	22.40
Boca de la Cañada	29.85	4.31	3.53	16.99	3.02	1.94	5.47	2.96
San Miguel Viejo	73.97	21.80	6.21	108.84	3.41	69.22	56.71	59.99
Nigromante	24.63	6.25	1.45	68.12	7.55	12.20	21.60	36.21

ND: Not detectable.

4.1.5 SUMMARY AND DISCUSSION

Based on the data collected it can be seen that in 8 out of 9 systems surveyed, the bacterial indicator and other elements measured were effectively reduced by the treatment system to safe levels for consumption. Total coliforms and COD in particular were found to reduce significantly throughout the system ($p<0.05$ and $p<0.001$, respectively)[19]. The important reduction of both parameters with the settling tanks ($p<0.05$)[20], which can potentially act as first-flush devices, is consistent with the literature (Kus et al. 2010; Yaziz et al. 1989; Abbott, Caughley, Ward, et al. 2007). The combination of filters with silver ions is shown to be effective in performing the additional removal required.

Although turbidity was not measured in this particular study, the visual aspect of the water was recorded and shown to consistently improve as it moved through the various points of the treatment system. Rainwater that looked yellowish and murky in the settling tanks, for instance, looked quite clear in the cistern and came out transparent after filtering and disinfection. This was the case for all sites.

The only failure (site #9) was caused by an identifiable leak that allowed cross-contamination by seepage from outside the cistern, a case which could certainly recur in future installations. This might imply that the purification system does not have the potency required for effective drinking water provision. However, the excessive bacterial load created by such situations could be addressed by increasing the levels of silver in the water. The devices employed for this purpose were set at approximately 5V; yielding residual silver concentrations lower than 5 ppb as described above. The equipment can reach up to a voltage of 20V, thus allowing a substantial increase whenever needed while still keeping within safe limits. WHO guidelines for drinking water quality conclude that concentrations of up to 100 ppb can be tolerated without risk, a value "under which no adverse health effects are observed" (WHO 2008).

[19] Evaluated using ANOVA tests for all points of the system from settling tank to drinking tap; $p[COD]<0.0005$; $p[coliforms]=0.0075$, using a $\log_{10}$ transformation for total coliform results

[20] Obtained by performing a two sample t-test, assuming unequal variances ($F>Fcrit$) where $p=0.041$

4.2 SECOND DATA SET – 2012

4.2.1 INTRODUCTION

As described in the methodology (3.2.2), the second round of fieldwork took place from September to October 2012, shortly after the start of the rainy season. In general terms, lessons learned were implemented, resulting in coordination and sampling efforts running more smoothly than in 2010, with the added advantage that rainfall had not been severe enough so as to impede access to the sites, as had happened during the first round.

Table 3.1 shows a list of the selected sampling sites for this period, along with location and general data on the systems. On this occasion, two sites which had been unavailable in 2010 due to maintenance (#10 and #11) were now functional and included in the study. Another system, San Antonio de la Joya (site #2), had problems with leakage in the cistern and was eliminated from this sampling round, bringing the total number of sites surveyed to 10 (up from 9 in the previous round).

4.2.2 FIELD MEASUREMENTS

Table 4.5 summarizes results obtained from main parameters analysed throughout the different sites and sampling points. The sampling points shown (number in brackets) are described in Table 3.4.

Conductivity in general terms was found to be low (in the range of 20-70 µS/cm) in the settling tanks, as is to be expected from rainwater which tends to have low dissolved solids. Conductivity increased sharply, however, in most systems at the tap or drinking water point, possibly partly due to the effect of the silver ionisation. COD was found to be moderate in the settling tanks and cisterns (10-40 mg/l) but was practically eliminated after passing through the purification system. TOC followed a similar pattern (Figure 4.3). Alkalinity values, on the other hand, tended to remain quite constant throughout the treatment process, but varied greatly within individual systems (10–80 mg/l), probably due to variations in roof composition. The leaching of calcium carbonate from poorly maintained concrete roofs could be a potential cause for increase (Morrow et al. 2010). The same applied to hardness, which was closely correlated to the alkalinity values.

Table 4.5. Means of main field parameters throughout the 4 sampling points

Parameter	**Settling Tank** [1]	**Cistern** [2]	**Ioniser** [3]	**Tap** [4]
Temperature (°C)	19.1 (0.5)[1]	19.5 (0.4)	17.6 (0.7)	19.4 (1.1)
pH	6.4 (0.1)	6.9 (0.2)	6.6 (0.2)	6.8 (0.1)
Conductivity (µS/cm)	43 (5.4)	138.2 (40.2)	100 (38.1)	145 (48.6)
DO (mg/l)	5.1 (0.3)	5.5 (0.2)	5 (0.4)	4.8 (0.3)
COD (mg/l)	14.4 (2.8)	8.6 (2)	13.5 (4)	2.3 (1.1)
Alkalinity (mg/l)	18.5 (1.9)	32.7 (5.6)	20.3 (3.9)	27.8 (4.6)
Hardness (mg/l)	23.5 (2.9)	40.4 (7)	25.6 (4.4)	42.3 (5.9)
TOC (ppm)	5.8 (2.04)	2.9 (0.5)	2.4 (0.5)	1.8 (0.6)
Silver (ppb)	NA	9.9 (3.4)	9.3 (5.7)	8.2 (3.6)

1. SEM: Standard Error of the Mean, cited in parenthesis. Maximum N=22, including repeats collected on different dates. Where a specific sampling point was unavailable, the corresponding N value was reduced.

pH was found to be close to neutral, and showed no significant variation throughout the different stages. The lowest value detected was 5.7 in one of the settling tanks, possibly due to the decomposition of leaves and the formation of humic acids (Meera & Ahammed 2006; Yaziz et al. 1989). The pH at the drinking tap was found to be above 6.2, which is in compliance with Mexican drinking water guidelines (Secretaría de Salud 1994). Water temperatures, measured directly on the field, were in the range of 19°C except for the intermediate silver ioniser point (3), which is enclosed within a concrete box together with the filters and pump, protected from the sun in a cooler environment.

Flow rates measured at the drinking water tap were an average of 1.0 litres/min, except in San Miguel Viejo (site #5 in Table 3.1) where values were slightly lower since this system is gravity-fed by an elevated tank, instead of a pressure pump like the other sites.

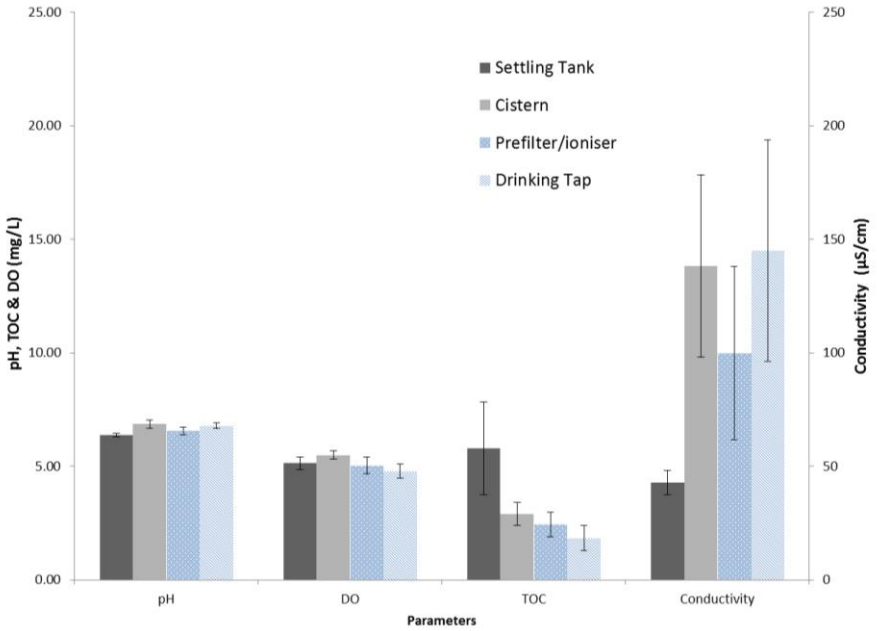

Figure 4.3. Comparison of selected field parameter means at each sampling point

4.2.3 MICROBIOLOGY

Faecal coliform counts were added as an additional bacterial indicator during this round, thanks to the availability of the specific broth at the SAPASMA lab (Table 3.2). Otherwise, analyses were performed using the same methods as before, with the advantage that on this occasion *E. coli* was properly counted and reported. Table 4.6 shows averages and range of values obtained using all microbiological indicators, in all the systems sampled and across the 4 sampling points. Wherever possible, repeat samples were taken on different days and used as an extra data point for the analysis.

As expected, and in accordance with results from 2010, settling tanks tended to have high bacterial counts, sometimes over 1,000 CFU/100 mL total coliforms, and correspondingly lower counts for *E. coli* (maximum value detected was 275 CFU/100 mL). However, after passing through the entire filtration and silver ionising system, counts were consistently reduced to zero, making the water safe for human consumption. As in the previous round, settling in itself tended to reduce bacterial counts (Table 4.6), which is in agreement with other studies performed on settling tanks and first flush systems (Kus et al. 2010; Doyle & Shanahan 2010), although not accounting for a total elimination, justifying the need for additional filtration and disinfection (Yaziz et al. 1989).

Table 4.6. Mean values of bacterial indicators (CFU/100 ml) across the sampling points

Coliforms	**Settling Tank** [1]	**Cistern** [2]	**Ioniser** [3]	**Tap** [4]
Total	618 (34 - 1450)	533 (2 - 1621)	75 (0 - 672)	4 (0 - 39)
E. coli	20 (0 - 275)	3 (0 - 41)	0	0
Faecal	41 (0 - 339)	60 (0 - 809)	0	0

Notes: Values in parenthesis represent range (min – max). Maximum N=22, including duplicates. Total number of sites = 10. Where N was lower it was due to unavailability of sampling points

It is noteworthy that a 100% elimination of all faecal indicators is obtained with the silver ioniser alone (Figure 4.4). Total coliform counts still show small numbers on some of the systems after final filtration (mean value = 4). This could be due to recontamination on the drinking tap or on the final pipelines, particularly, where tubes are under the sun and the systems are not used for a prolonged period. Presumably, this could be diminished by flushing for longer before sampling or drinking (though this was not tested). In some cases, where very low colony counts are present (i.e. ≤ 4) it could also be due to cross-contamination or errors during the analysis itself.

4.2.4 SILVER IONS AND CHEMICAL COMPOSITION

Average concentrations of silver ions from the cistern to the drinking tap are included at the bottom of Table 4.5. These were measured by ICP-MS using acid-preserved samples, as described in the methodology (3.2.4.3). Values detected at the drinking water points were all well below the 100 ppb limit set by local and international guidelines (WHO 2008; Secretaría de Salud 2000). As discussed previously, these dosages are not known to be harmful nor toxic to human beings. The maximum reading obtained was 57 ppb, with average values around 10 ppb. Some silver was also found to 'backflow' into the cisterns, providing extra protection from recontamination. This could be partly due to the fact that the sampling valve for the cistern was located at the outlet (i.e. the pipe that conducts water to the pump and purification system). Since this pipe is physically located at a lower level than the ioniser and drinking tap, it can be inferred that, particularly in periods of inactivity, some water and thus silver ions will flow back by gravity.

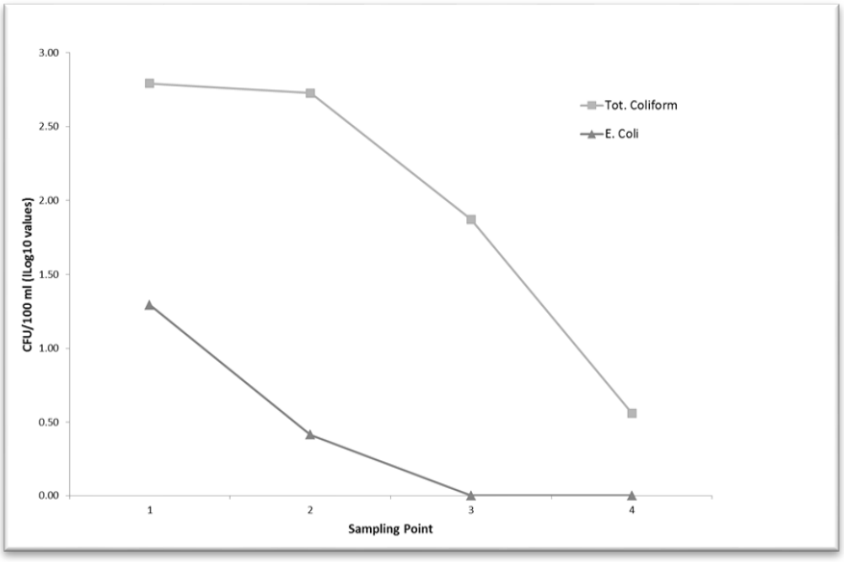

Figure 4.4. Reduction of average total coliforms and *E. coli* (log_{10} values)

Anions and cations (Table 4.7) were present in low concentrations throughout, with the highest anions being nitrate and sulphate, possibly due to atmospheric precipitation of acid compounds (Appelo & Postma 2005). Correspondingly higher concentrations of total sulphur were also recorded, as expected from rainwater. Furthermore, calcium and sodium values were slightly higher than those for other cations, most likely due to concrete roofs and a corresponding increase in hardness.

Table 4.7. Mean concentration values[1] of selected cations and anions (mg/l)

Anions	**Settling Tank** [1]	**Cistern** [2]	**Ioniser** [3]	**Tap** [4]
Cl	1.88 (0.47)	3.61 (1.22)	2.3 (1.3)	3.6 (1.7)
NO_3	5.51 (1.94)	10.94 (2.92)	12.4 (4.2)	10.4 (5.3)
PO_4	0.74 (0.28)	1.42 (0.84)	0.3 (0.2)	0.2 (0.1)
SO_4	8.94 (3.39)	10.8 (2.14)	7.1 (2)	11.8 (2.2)
Cations				
Ca	5.01 (1.26)	9.6 (1.59)	7 (1.4)	10.5 (1.6)
K	0.81 (0.35)	3.74 (1.16)	2.9 (1.6)	3.7 (0.8)
Mg	0.14 (0.02)	1.75 (0.99)	0.7 (0.3)	1.2 (0.3)
Na	0.55 (0.34)	12.83 (5.74)	7.9 (5.6)	11 (5.1)
S	1.11 (0.24)	3.07 (0.69)	2.1 (0.5)	4.3 (1.1)

1. SEM values shown in parenthesis. Maximum N=15, including duplicates.
Phosphorus (P) and fluoride (F) not shown as only trace amounts were found

4.2.5 *SUMMARY AND DISCUSSION*

The data obtained confirms and improves upon the findings of the first round of fieldwork, namely the effectiveness of the treatment system as a whole in removing bacterial indicators, as well as improving on general water quality parameters. The treated rainwater had good visual aspect and reportedly agreeable taste (Figure 4.5). Silver was also measured to be present in most samples within acceptable limits, including in cisterns, suggesting a 'backflow' of ions. It must be noted, however, that the field studies as a whole are based on a limited number of samples, and conclusions inferred from these must be treated with caution (see section 6.3.2 for a detailed discussion on this). Maintenance issues are also observed, with a few of the systems not operating properly or not being used at all (this is covered more thoroughly in section 6.4).

Figure 4.5: Sampling detail at the drinking water tap

The following chapter consists of results obtained during the course of the laboratory research that took place at University College London after the first sampling round of 2010. The setup of filters, ioniser and other components in the field was used to inform the initial experimental arrangements performed in the lab.

5 LAB RESULTS

This chapter presents a compendium of lab experiments performed along with the main results obtained. This is complemented by Annex A, which lists a record of all variables, data points and measurements. The results and discussions shown below are categorised according to the particular lab model used (summarised in Table 3.12).

5.1 BATCH EXPERIMENTS

Batch tests are further classified according to the method or device used for dosing silver (see 3.3.1.1 for a full description).

5.1.1 HALF-CELL DEVICE

Initial tests were performed to determine the silver concentration achieved by this 'floating' device in DI and rainwater, as well as the stability of the ions over time. The silver solutions generated were also used for other experiments where direct contact with the actual device was undesirable, such as bacteriophage tests (0).

5.1.1.1 Ionisation capacity

Table 5.1 summarises the main results of batch experiments performed using this device. It can be observed that the silver concentration level reached in solution varies highly depending on the test water used, which is closely correlated to conductivity. For the sake of comparison, a new variable was defined for this research, not used in the literature previously, which was given the name of Ionisation Capacity (IC), defined as 'the total amount of silver (in µg) generated in a solution per volt applied to the electrodes, per minute'. It acts as a normalising variable, grouping together voltage, volume, time and silver concentration.

Table 5.1. Comparison of ionisation capacities across a range of water conductivities

Water	**Cond.** (µS/cm)	**Volume** (ml)	**Ionisation time** (min)	**Voltage** (V)	**Silver**[2] (ppb)	**IC** (µg/V.min)[3]
DI	0.7	300.0	5.0	9.97	27.3	0.16
DI	0.7	300.0	11.0	9.97	44.2	0.12
RW	52.5	300.0	11.0	9.97	820	2.2
RW[1]	170.0	750.0	17.5	10.18	670	2.8
TAP	670.0	500.0	7.0	10.00	940	6.7

1. RW samples taken on different dates, which incidentally allowed for a better conductivity 'gradient'
2. DI samples analysed with ICP-MS, due to expected low concentrations; rest used spectrophotometry
3. Total amount of silver dissolved (µg) = concentration (ppb) x Volume (ml) / 1000
Note: ppb is equivalent to µg/l

The conductivities shown correspond to the raw water used for the experiment, before starting ionisation. Variations during the course of ionisation were shown to be minor, possibly more attributable to instrument imprecision than to any significant change, and are thus not displayed. For instance, in the case of tap water (last entry on the table), conductivity showed a *decrease*, after 7 minutes, instead of the expected increase (due to the release of more ions into the water), down to a reading of 658 uS/cm. However, on a 2nd reading of the same liquid a value of 680 was obtained (using a Jenway 4330 meter). These are not important drifts if seen percentage-wise. Significant changes in conductivity would probably only be detected for much higher relative values of new (Ag+) ions vs. those already existing in the water (Section 5.5.1). pH, on the other hand, was seen to vary for tap water upon ionisation, from a starting value of 8.1 to 8.5 after concluding. For DI and RW, however, no significant change was observed, from the initial pH values of 5.5 and 7.1, respectively. The issue of pH variation is further explored and discussed in 5.5.2.

Overall, results show a marked increase in ionisation capacity with rising water conductivity, which is directly proportional to the electric current passing through the anode, leading to a greater release of silver ions (Landau 2007). This is shown in Figure 5.1. However, care must be taken in interpreting the highest tap water value (940 ppb)[21], as silver saturation could have been achieved before the experimental ionisation time (7 min). This saturation level compares to other results obtained using silver rods (5.1.3). The ensuing IC variable would be considerably increased if the time to reach the same Ag concentration were reduced. Despite the above limitation, the general principle of greater ionisation capacity with increasing conductivity is still illustrated with the experiment.

[21] These values are outside the linear range of the instrument (>700 ppb). Although readings can be considered to be good estimates, accurate measurements cannot be entirely guaranteed.

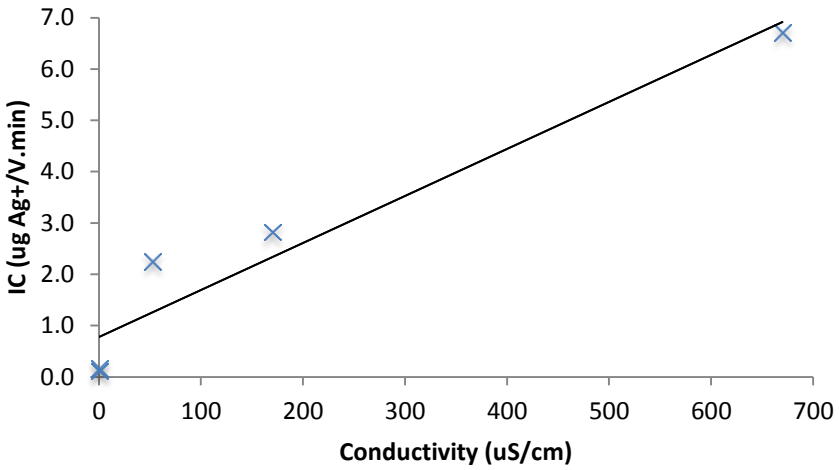

Figure 5.1: Plot of Ionisation Capacity (IC) vs. conductivity, with trendline (y=0.0092x +0.77)

Table 5.2 summarises visual observations recorded during these and other batch experiments. Turbidity measurements were taken for some samples, since particularly for tap water there are marked variations. These merit a separate discussion (5.5.4) and are further tested using Model II (continuous flow), which was specifically set up to investigate variations in turbidity with electrolytically generated silver concentrations.

Table 5.2. Visual observations during the ionisation process for different test waters

	DI	RW	Tap
Anode (+)	No apparent change observed	White 'cloud' observed, takes longer to form and in lower intensity than tap water.	Almost instant white 'flume' observed going downwards and precipitating to bottom of container
Cathode (-)	Very small bubbles observed after a few minutes	Small bubbles observed around electrode after a few minutes	Fizzing strongly (bubbles), possibly Hydrogen (Delahay et al. 1951)
Water condition (visual)	Stays the same - transparent	Becomes slightly whitish and turbid after several minutes	Becomes turbid/white rapidly, with a purple sediment collecting at the bottom

5.1.1.2 Comparison with Ag/Cu device

For the following experiment, a device made from a silver/copper alloy (3.3.1.1) was utilised for comparing performance with the half-cell device, made from pure silver. The mixture of silver with other metals such as copper, which has disinfection properties in its own right, is often proposed in the industry as a cost-effective alternative (Landau 2007; Health and Safety Executive 2013; Landeen et al. 1989).

Some basic tests were thus made, imitating as closely as possible the experimental conditions described in the previous section.

The volume for all tests was fixed at 300 ml in a glass beaker. Results are shown in Table 5.3. Voltage applied was constant, at 9.97 V, to enable an accurate comparison between both devices. Conductivities, in µS/cm, were 0.7 and 52.0 for DI and RW respectively. The pH of RW was measured to be 6.4. These tests were all performed on the same day with samples analysed using ICP-MS (see footnote at bottom of Table 5.3).

Table 5.3. Comparison of copper alloy and pure silver cells (Ag values in ppb)

Time (min)	Cu/Ag		Half-cell (pure Ag)	
	DI	**RW**	**DI**	**RW**
0	0.0	0.0	0.0	0.0
5	0.8	8.8	27.3	NA
10	3.3	NA	44.2	>700[1]

1. ICP-MS reading was well above calibration range, even after 1:10 dilution). Value shown was measured using Hach spectrophometer (over measurement range).

Figure 5.2 shows these results graphically. As expected, the copper-containing unit produces considerably less silver ions than the half-cell silver device, with both highly dependent on water conductivity, as discussed in the previous section.

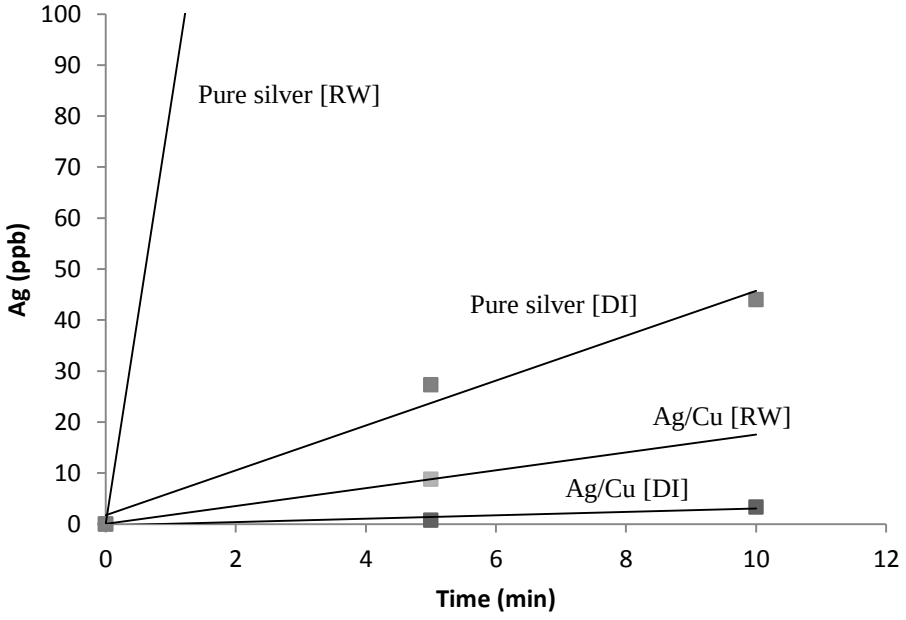

Figure 5.2. Simplified graph of data in Table 5.3 (showing trendlines for visual comparison). Highest silver value (Ag>700) not shown.

5.1.1.3 Disinfection

Disinfection experiments with the half-cell device were mostly performed by ionising water separately in order to produce a concentration of silver ions, and then applying it to a solution containing bacteria or viral particles (Sections 5.3.2 and 5.3.3). The following experiment was done by applying (i.e. floating) the device directly in a volume of pre-contaminated water:

In a glass beaker, 200 ml of unfiltered RW were inoculated with 0.5 ml of WG-5 *E. coli* (estimated concentration of 10^6 CFU/ml – see 3.3.5.2 for details). After stirring for 5 min, a control sample was taken, followed by 20 min of ionisation using the half-cell device (V = 4.97V), powered by an Arduino supply (3.3.1.3) set to a 'switching' period of approximately 15 sec. Samples were analysed in duplicates, using the Coliblue® membrane filtration method, obtaining the results (after 24 hour incubation at 37ºC) shown in Table 5.4.

Table 5.4. Bacterial disinfection in RW using the half-cell device

Sample	**Silver (ppb)**	**E. coli** (CFU/100 ml)	**Total coliform** (CFU/100 ml)
Control (t=0)	0	TNC	TNC
After ionisation (t=20 min)	>700[1]	0	0

1. Measured with Hach spectrophotometer (reading over measurement range)
2. Too numerous to count, after dilutions (estimated at 10^3 - 10^4 CFU/ml)

A complete elimination of the indicator bacteria can be observed, with high silver doses generated at a voltage close to that commonly used in the field (5V). This might simulate stagnant conditions (i.e. no flow), where high concentrations of microorganisms could accumulate, such as in a biofilm forming along a pipe, for instance. The effectiveness of silver in controlling biofilms, which are more resilient than the non-aggregated bacteria inoculated in this experiment, has been tested previously by Silvestry-Rodriguez et al. (2008).

5.1.2 FULL-CELL DEVICE

This device was designed specifically for continuous flow experiments, and as such few batch experiments were performed on it. An initial determination of silver ionisation capacity yielded the following results (Table 5.5), which are useful for comparing with other batch experiments, using different amounts of silver.

Table 5.5. Ionisation Capacity of full-cell device in selected batch experiments

Water	**Cond.** (µS/cm)	**Ionisation time** (min)[1]	**Voltage** (V)	**Silver** (ppb)	**pH**	**IC** (µg/V.min)[2]
RW	135.0	5.5	5.00	300	7.4	3.3
TAP	673.0	5.1	5.00	>700	NA	9.1

1. Times are approximate, with minor variations occurring due to manual delays in opening valves, etc.
2. Total amount of silver dissolved (µg) = concentration (µg/l) x 0.3 L; where 0.3 litres (300 ml) is the volume of the ionising vessel (3.3.1.1). Note that ppb and µg/l are equivalent units.

It can be noted that the ionising capacity (IC), defined in the previous section, is considerably higher using this device, as compared to the half-cell device (Table 5.1). An important variable to consider here is the amount of metallic silver actually in contact with the test solution, which will influence the current flowing through the electrodes and the rate of ions released (Roberge 2012). Assuming all silver cells have the same degree of purity this can easily be determined by calculating the volume of the silver cell submersed in water at any given moment. In the case of the full-cell device, the volume of each coin is roughly 3.8 cm^3 (see Table 3.5). This compares well to the industry standard for pure silver which specifies a density of 10.5 g/cm^2, yielding an approximate weight of one ounce[22] per coin, as expected.

For this particular device, the entire surface of the cells are in contact with the water, in contrast with the half-cell device, where part of the cell is covered in waterproof sealant (Figure 3.7), decreasing the actual submersion volume. Out of the 4 cm diameter of the coin, only about 2 cm are immersed in water for each experiment, corresponding to 0.9 cm^3 of metallic silver volume.

5.1.2.1 Natural silver ion release in water

An issue which arises frequently in the literature is the idea of passive release of ions from metallic silver (i.e. without electricity). It is known that the American pioneers would place a silver coin into their milking jugs to keep it sterile, and that the ancient Egyptians as well as other civilizations favoured the use of silver vessels purportedly to conserve their drinking water (Wesley Alexander 2009). Due to the simplicity involved, there is an understandable attractiveness in applying the disinfection capacities of silver without the paraphernalia of a power supply and a control circuit.

[22] Silver density calculations taken from http://goldsilvertools.com/densimeter/

An experiment was performed to test the passive release of ions after a day. The full-cell device was left inside the ionising vessel, which was filled to the top (approx. 300 ml) with DI water. Conductivity was measured to be 0.8 µS/cm. Samples were taken at the start and after 24 hours. It was observed that silver increased from 0 to 7.2 ppb (analysed by ICP-MS), confirming that there is a passive release even in the extreme case of low conductivity water. Presumably, this would be higher for RW and Tap water, with increasing conductivities, as shown for the ionisation experiments performed (see Sections 5.1.1.1 and 5.5.1).

Silver foil in contact with rainwater was also shown to reduce coliform counts substantially, albeit in low volumes (less than a litre) and with a considerable surface area of silver foil submersed in the container (Thomas et al. 2010). Passive application such as these, though apparently cost-effective, are probably not suited to higher demands where flow is involved and a stringent safety standard is desired. The experiment does prove, however, that even in the case of power failures in the systems, a limited disinfection capacity will still be achieved by the device.

5.1.3 SILVER RODS

Silver rods were prepared as described in the methodology (3.3.1.2). These were used mostly for electric current experiments, given the ease with which they could be moved and shifted within the test waters. Some evaluations were also done on silver ionisation capacity, with the main results shown in Table 5.6. All these tests were done in glass beakers, with the volume kept fixed at approximately 850 ml and the voltage as constant as possible (near 5V). Ionisation Capacity (IC), as described in Section 1.1.1, is used as a standard variable for comparison of the silver ion 'yield' per time, for a given voltage and water conductivity.

Table 5.6. Ionisation capacity of silver rods (Ag measured with Hach spectrophotometer)

Run No.	Water Type	**Conduct.** (µS/cm)	**Voltage** (V)	**Time** (min)	**Silver** (ppb)	**pH**	**IC** (µg/V.min)	**Dist**[1] (cm)
1	DI	3.0	5.00	230.0	706	6.1	0.55	4.0
2	RW	79.5	4.96	4.0	650	6.5	26.2	2.5
3	RW[2]	80.7	4.90	4.5	230	6.5	8.3	2.5
4	RW	94.0	5.00	32.0	805	7.1	4.5	7.5
5	RW	94.0	5.00	71.0	730	NA	1.7	7.5

1. Refers to distance between rods for that particular experiment
2. Ionisation done with 'switching' voltage supply (every 15 sec). All other tests used fixed supply

Conductivity and pH values shown on Table 5.6 refer to initial readings, since they did not vary significantly during the course of experiments, as described in Sections 5.5.1 and 5.5.2. Lines 4 and 5 (shaded in grey) represent one continuous experiment,

while the other runs were performed on different dates (thus the differences in conductivity for RW).

As in the case of other devices tested, the ionisation capacity (IC) is considerably lower in DI than in RW, given the large differences in conductivities. The differing IC values in the case of the continuous RW experiment, however, suggest that a peak or 'saturation' value seems to have been reached in the fixed volume of rainwater, possibly around 800 ppb. The fact that the second reading (time = 71 min) shows an actual drop in silver concentration compared to the first one, should not lead to any particular conclusions, as both readings are above the measuring range of the instrument used (>700 ppb) and can only be considered best estimates. It could also be possible that the saturation value could have been reached much before, judging by the second row on the table, where a silver concentration of 650 ppb is reached in only 4 minutes, at a slightly lower conductivity. More frequent samples and more detailed analysis would have been required to better determine this saturation effect, which is not considered a critical factor in the current context of continuous flow.

Runs #2 and #3 in Table 5.6 merit a special discussion. A close inspection reveals that, despite all conditions being very similar (conductivity, pH, ionisation time, etc.), run #2 yields a silver concentration of 650 ppb, while run #3 only 230 ppb. This marked difference is related to the different power supply used, a phenomenon which was found to be an important contribution of the present work, discussed in more detail in section 5.4.5.

5.1.4 STANDARDS

Silver standards were utilised mostly for experiments dealing with the stability of silver ions in water (Section 5.1.6), for bacteriophage testing (Section 0) and for the bacterial disinfection experiments described below.

5.1.4.1 Microbiological response to silver standard

For the following experiment, 800 ml of rainwater were collected in a sterile open glass beaker and inoculated with 100 µl from a vial of concentrated *E. coli* (theoretically achieving 5 x 10^4 CFU/ml after inoculation). After 10 min, 40 µl of a Hach-Lange silver standard solution (1,000 ppm) were pipetted into the mix. This would produce a theoretical final concentration of 50 ppb, assuming no precipitation or complexing of silver ions. Samples were taken for bacteria (total coliforms, *E. coli*) and silver after 5 and 20 min, respectively. Sample R0 corresponds to the raw RW

sample used for the experiment, with the following basic parameters: Conductivity = 50 µS/cm[23], Temperature = 25ºC and pH = 6.7. Results are summarised in Table 5.7.

Table 5.7. Interaction between E. coli and silver standards in RW

Sample	Time (min)	Ag 107 (ppb)[1]	Coliform total[2]	*E. coli*
R0	Initial	NA	8	0
R5	5	0.9	TNC	TNC
R20	20	0.6	[3] 54	0

1. Silver analysed with ICP-MS the following day, according to standard procedure
2. Bacteria measured using Coliblue® broth, expressed in CFU/100 ml
3. This result could be due to cross-contamination, as colonies were located on the filter's edge

E. coli was absent and only a few total coliforms found in raw rainwater from the barrel, which was expected (see III, 3.3.2.1). After spiking, an uncountable number of colonies (TNC) were detected, even after successive dilutions, covering the entire filter upon analysis after a 24 hour incubation period (presumably >10,000 CFU/100 ml). According to the controlled experiments performed with the same standards (Section 5.1.6.1), under similar conditions, silver concentration should have been theoretically close to 40 or 50 ppb, had there been no bacteria added. The sample taken after a few minutes shows a near complete drop in Ag concentration, without a full disinfection (the exact reduction could not be determined as more dilutions would have been needed). It is presumed that all the silver is absorbed by the large presence of bacteria, retained in their cell walls and reacting with any released organic matter (Jung et al. 2008; Gerba & Thurman 1989). However, all *E. coli* are completely inactivated after 20 minutes, with an accompanying further drop in free silver ions down to almost undetectable levels.

Anions were also measured before and after the experiment (Table 5.8) showing a very low variation in anions resulting from the silver and *E. coli* addition, not in any significant levels. A small drop occurs in chloride and nitrate concentrations, presumably due to the formation and precipitation of silver chlorides and nitrates. Due to the relatively low amount of silver present, however, the change in resulting concentration is barely noticeable. The standard itself contains nitric acid, used for

[23] Measured with ECTestr low range portable conductivity meter

preservation, but this does not seem to have any noticeable effect either, perhaps given that only 50 µl were applied.

Table 5.8. Selected anions (in mg/l) from silver standard experiment in RW

Sample	Cl	NO_3	SO_4
R0 (pure rainwater)	2.9	10.0	16.4
R20 (after 20 min)	2.4	9.6	16.4

Note: phosphate, fluoride and nitrite also analysed but not detected

Silver standards were also measured in the lab to test their effect on algal growth in RW. *Chlorella sorokiniana*, a green-algae strain, was shown to be inhibited at concentrations of 100 ppb, reducing growth down to 80% from initial levels, with a complete inhibition at 200 ppb (Jin 2012). These concentrations have been shown to be achievable with the devices used for the present research.

5.1.5 ION DIFFUSION

5.1.5.1 Vertical diffusion in glass column

A vertical column was set up as described in 3.3.4.1, with the aim of measuring the ability of electrolytically generated silver ions to travel upwards through a water column or pipe. Silver ions were generated in DI using the half-cell device (3.3.1.1), up to a 640 ppb concentration, measured with spectrophotometry (5.1.6.1). 50 ml of this solution were added to the bottom of the column, gently pouring 450 ml of RW on top without stirring or causing any turbulence (which would have affected the results). The proportion was thus 1:10, which would theoretically give a final concentration of 64 ppb, assuming homogenous mixing and no elimination of silver ions through precipitation or complexing.

After exactly 1 minute, a sample was carefully taken from the top of the column, obtaining the following results (silver measured using Hach spectrophotometer):

Conductivity = 60 µS/cm
pH = 6.5
Ag = 20 ppb

These preliminary results confirm that the silver ions are capable of ‘travelling’ upwards, against gravity, in relatively low conductivity rainwater. The following experiment examines this phenomenon in more detail.

5.1.5.2 Interconnected beakers

The setup for this experiment is described in 3.3.4.1. In contrast to the test described above, the means of diffusion here consists of a thin rubber tube, connected to a glass outlet at the bottom of each beaker. This will have the effect of forcing the free ions into a narrow surface, where the possibility of interacting with precipitating anions is greater. In addition, the possibility of increased contact exists with the glass on the small, tubular outlets, which could be a cause for further precipitation as silver ions may tend to adsorb onto glass surfaces (APHA 2012; Struempler 1973). The silver concentrations for Beaker A (Table 5.9) were all obtained by ionising with the 'floating' half-cell device (Figure 3.6) for 5 – 10 minutes.

Table 5.9. Ion diffusion in interconnected beakers (Vol = 400 ml; Temp =24 ºC) [1]

			Beaker A (ioniser)		**Beaker B (control)**	
Water Type	Conduct. (µS/cm)	pH	Silver (ppb)	Turbidity (NTU)	Silver (ppb)	Turbidity (NTU)
DI	2.0	5.6	140	0.07	20	0.07
RW	122	NA	830	31	<10 [2]	4.7
Tap	670	8.6	940	NA	0	NA

1. Voltage set at approximately 5V (using fixed power supply)
2. Reading below detection limit of Hach instrument. 5.6 ppb were obtained using ICP-MS

The results show clearly that as conductivity increases, there is less silver ion diffusion from one container to the other, as expected due to the higher presence of free anions. Furthermore, a correlation can be observed with turbidity in RW. As described in Table 5.2, water being ionised turns 'cloudy' and turbid (except for DI) in a relatively short period of time. Thus, turbidity variations can be used as an indirect indicator of silver generation, as long as measurements are taken soon enough after ionisation, before any particle settling occurs. This is discussed in section 5.5.4.

5.1.6 STABILITY AND DECAY OF SILVER IONS

In order to test the residual time of silver ions in water, a factor of importance in the field, the following experiments were performed. Electrolytic generation of silver ions (i.e. using the devices) was compared to the use of liquid silver standards, which are usually stabilised in a nitric acid solution and could thus have a different behaviour, as described in 3.3.1.2. Comparisons were also drawn in both cases between RW and deionised water (DI).

5.1.6.1 Electrolytic generation

The first test consisted of ionising 1 L of DI in a clean glass beaker with the half-cell device (Figure 3.6), using the original 'switching' power supply (see 3.3.1.3) at its maximum voltage setting (12.7 V). After an ionisation time of 25 min, the beaker was covered and stored at 20°C in the dark. This was also used a stock solution for the proceeding experiments. Silver was monitored regularly for over a month to test for decay, as shown in Table 5.10.

A second test was done in RW by adding 100 ml of the 'stock' solution described above to 900 ml of fresh rainwater collected from the butt (in a 1:10 dilution). This new solution (also 1 L) was covered and stored under the same conditions, monitoring silver at more regular intervals since, as expected, decay occurred more rapidly due to the presence of chlorides and other potentially precipitating particles (Table 5.11).

Table 5.10. Stability of silver ions in deionised water (DI)

Day	**Ag** (µg/l)	**Conductivity** (µS/cm) [3]	**pH**
Initial[1]	0	<10	NA
0 [2]	620	110	NA
3	670	110	NA
5	650	110	6.5
10	640	110	6.5
11	640	110	7.0
47	600	110	NA

1. Values obtained in the raw DI water before the addition of silver (i.e. blank)
2. Reading obtained right after silver addition. All samples analysed with Hach spectrophotometer
3. Measured with a low resolution ECTestr meter (detection limit = 10 µS/cm). Note conductivity increase upon addition of standard (see 5.5.1)

The apparent increase in silver concentration on Day 3 (Table 5.10) is probably due to an inconsistency in the methodology: the solution was stirred before analysing on this day, while for the rest of the samples it was not stirred, according to a previously established procedure. Stirring would potentially move or re-dissolve any silver containing sediments or precipitates, increasing the concentration being read.

Table 5.11. Stability of silver ions in rainwater (RW)

Day	**Ag** (µg/l)	**Conductivity** (µS/cm)	**pH**
Initial	0	70	6.5
0	80	80	NA
1	60	70	6.6
2	30	70	6.6
3	10	70	6.9

Note: test started on day 10 of previous experiment (Table 5.10), when Ag≈640 ppb

Conductivity is seen to increase slightly after adding the silver solution to RW and then decrease. However, the instrument used for this experiment (ECTestr) is of

limited accuracy as it only reads in 10 µS/cm increments (3.3.5.1). Better instruments became available for successive experiments. Another factor to consider is the total volume of water in the vessel, which decreased for every sample (50 ml required for each silver test), potentially increasing the concentration of dissolved or suspended solids, partially affecting conductivity or other parameters.

Figure 5.3 shows a comparison of the silver ion decay in solution between both test waters. After 3 days, silver concentration in the RW had dropped down to 87% of its original value (80 ppb), while silver in DI perceived a mere 4.5% loss from its highest value in 11 days. Despite the few RW samples taken (n=4), regression analysis yielded a strong linear drop, with r = 0.99 and p<0.005 (one-tailed), with a slope of m = -24 ppb/day. In other words,

$$\boldsymbol{Ag\ (ppb) = -24D + Ag0} \qquad [5.1]$$

Where D refers to the number of days after silver addition and Ag0 to the initial silver concentration. Equation 5.1 cannot be generalised, however, except for the particular case (Conductivity≈ 70 µS/cm, Ag0=80 ppb and starting experimental volume of 1 L). Furthermore, it doesn't provide data on the effect of other factors, such as the presence of interfering ions, organic matter or suspended solids. It can serve as an estimated guideline, nevertheless, since this conductivity is fairly typical of the RW systems in the field (Table 4.5). More samples would be required to adequately construct a generalised model.

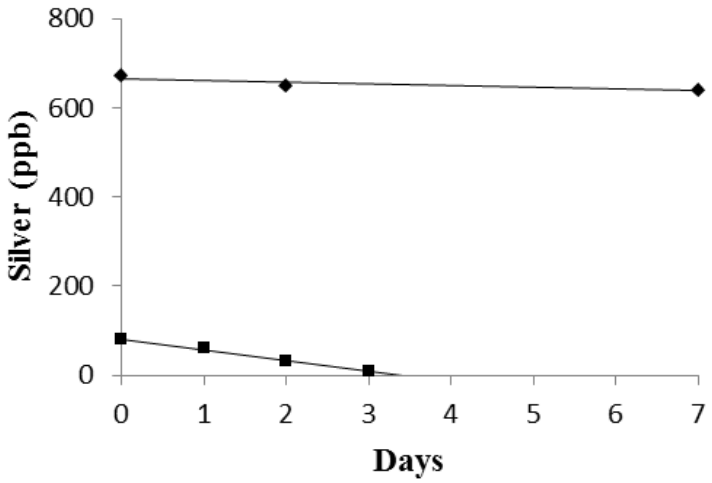

Figure 5.3. Silver residual in test waters (DI and RW). Ag DI values assumed to be starting on Day 3 for graphical comparison

Stability in tap water

On a separate experiment, 700 ml of tap water were ionised in a glass beaker, using the half-cell device for 22 min, with a 'fixed' power supply set at 10V. After 24 hours silver was measured, obtaining the results in Table 5.12. A silver ion decay of 13.2% is observed (although both values are over the linear range of the Hach spectrophotometer used).

Table 5.12. Silver ion decay in tap water

Day	Ag (ppb)
0 (after ionisation)	910
1 (after 24 hours)	790

Note: Initial conductivity = 531 µS/cm

5.1.6.2 Standards

The decay of silver ions was tested using a 1,000 ppm silver standard (Hach-Lange), in both ultra-pure Milli-Q water and RW (water sources are described and characterised in 3.3.2). Silver analyses were done using the Hach spectrophotometer (see Table 3.10), except for lower concentrations where ICP-MS was used.

Milli-Q Water (MQ)

A 500 ppb solution was prepared by adding 50µl of silver standard to 1 L of MQ in a glass beaker. Table 5.13 shows initial silver readings and after 10 days. The long time elapsed between both samples was based on results from the previous experiment (5.1.6.1), where it was shown that there was very little silver decay in DI (and presumably MQ water is purified to a higher standard).

A drop of 10 ppb was observed after this period. Given the instrument resolution (±5 ppb), these measurements could potentially be much closer to each other. Measurements using ion chromatography revealed all major anions to be below the detection limit, except for nitrate (NO_3 = 0.71 mg/l), this small increase possibly due to the presence of nitric acid in the silver standard.

Table 5.13. Silver ion stability from Ag Standard in MQ water

Day	**Ag** (ppb)
0	50
10	40

Rainwater (RW)

Silver residual was tested for different mixtures of rainwater and silver standard as follows:

a) The 1,000 ppm standard was serially diluted in MQ down to a concentration of 500 ppb. From this solution, 100 ml were poured onto 900 ml of RW collected from the butt, for a (theoretical) final concentration of 50 ppb (i.e. a 1:10 dilution). Silver was measured periodically as shown in Table 5.14. Anion measurements were also done on both a blank (pure RW) and the sample after silver addition (Table 5.15).

Table 5.14. Silver decay using standard in RW

Day	**Ag** (ppb)
0	40
4	<10 [1]
6	0

1. Reading below instrument detection limit.
Although a presence of silver is confirmed, exact value could not be determined.

Table 5.15. Anion concentrations (mg/l) before and after silver addition

	Cl	NO^3	SO^4
Pure RW sample	2.99	10.08	14.81
With silver (40 ppb)	3.00	9.95	15.23

Ion chromatography was repeated 2 weeks later using 50 ml of rainwater (from a new batch) and preparing in a similar manner, obtaining a final concentration of 50 ppb of silver. Results were more congruent than the previous ones (Table 5.16), as small decays in the three major anions measured are to be expected due to their complexing with silver ions. Differing values in the original experiment could be partly due to the IC instrument, which displayed some erratic readings in the first analysis.

Table 5.16. Anion measurement (mg/l) rerun with silver standard addition

	Cl	NO^3	SO^4
Pure RW	2.14	6.75	4.46
With silver (50 ppb)[1]	1.78	6.53	3.63

1. Silver measured with Hach spectrophotometer, 5 min after adding standard

b) Another experiment was performed for lower silver concentrations. From the same 500 ppb diluted Ag solution prepared as shown above, 1 ml was added to 99 ml of RW (1:100 dilution), for a theoretical final concentration of 5 ppb. Due to the detection limit of the Hach instrument, only ICP-MS was used on this occasion to measure silver. Anions were also analysed (Table 5.17.).

Table 5.17. Silver decay for low concentrations of standard in RW

Day	Ag (ppb)	Cl	NO^3	SO^4
0	2.8	2.99	9.96	14.68
1	2.3	2.98	9.66	14.90

Note: anion concentrations in mg/l

Even in such low concentrations, a relative silver drop can be observed in RW after one day. However, no significant changes seem to occur in anion composition upon the addition of the silver standard.

5.1.6.3 Effect of nutrient load

An MSc student investigating the effect of silver ions on algae, working under the author's supervision (Jin 2012), performed the following experiment in order to test the effect of adding a nutrient stock[24] to the decay of silver ions in RW (Table 5.18).

Bottle A contained 1,000 ml of RW + 0.2 ml of silver standard (1,000 ppm), obtaining a resultant initial concentration of 200 ppb Ag. Conductivity was initially measured to be 273 µS/cm and pH = 7.1, with no significant variation in either parameter throughout the sampling period. Initial nutrients in the RW were low, as expected: NO_3 = 2.1 mg/l; PO_4 = 0.8 mg/l (measured by ion chromatography).

Bottle B contained the same amount of silver standard, but with the addition of 20 ml of the nutrient solution (adjusting the rainwater quantity accordingly in order to obtain the same 1,000 ml total volume). Upon addition of the nutrient stock, conductivity increased to 1941 µS/cm. pH remained at a similar value of 7.2. NO_3 increased correspondingly to 22.5 mg/l and PO_4 to 25.5 mg/l.

Table 5.18. Silver concentrations (ppb) with increased nutrient load

Day	Bottle A (control)	Bottle B (nutrients)
1	200	200
2	120	70
3	60	20
6	40	10
7	30	10

Results confirm a faster decrease in the rainwater with a higher nutrient load, compared to the pure RW samples, as shown in Figure 5.4. It is possible that silver

[24] Bold modified basal, commonly used for growing algae

nitrates or other precipitates could be forming, leaving less free silver ions for disinfection, which has obvious practical implications. Nutrient loading could occur in a rainwater system where leaves, organic matter or agrochemicals are present, if they are not adequately filtered out before reaching the storage tank (Kus et al. 2010; Kim et al. 2005). The same experiment was repeated for aerated samples (with a constant injection of oxygen) obtaining similar results (not shown here).

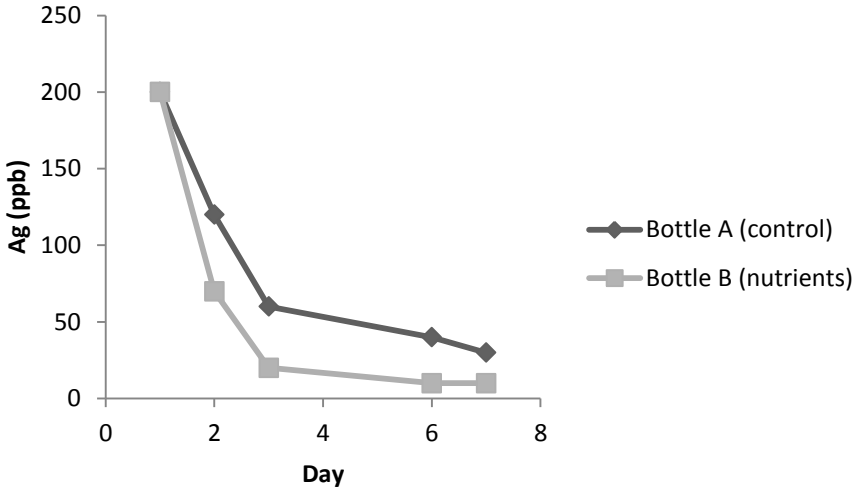

Figure 5.4. Silver ion decay comparison with and without nutrient loading in RW

5.2 CONTINUOUS FLOW

5.2.1 MODEL I

The setup for this model, designed to emulate the systems in the field, is described in 3.3.3.1. Only RW was used as a test water source. Sampling point numbers are shown in Figure 3.13. The silver ioniser (full-cell device) was added to the model between the pre-filter and the final filters (sampling points 2 and 3). Silver ions were not detected upstream in any of the ionisation experiments. In other words, a 'backflow' of ions was not observed under continuous flow operation (see 5.1.5 for a discussion on ion diffusion in batch experiments). For this reason, only points 3 and 4 are shown in the results below ('downstream' from the ioniser).

5.2.1.1 Ionisation capacity

The following tables summarise the experimental runs performed, varying parameters such as flow and sampling time. Voltage was kept basically constant, at approximately 5V, which is the setting most commonly used in the field. Results are classified according to the power supply used (3.3.1.3), as this was seen to have an effect on silver ionisation capacity (5.4.5). For the sake of clarity, numbers in the 'Run' column represent independent runs, while the letter subscripts refer to samples collected at different times within the same experiment. The sequence in which they

were performed is also maintained, as it affects the level of silver saturation that seems to be occurring in the filters, as explained below.

Initial ionisation tests were performed with the SilverLife unit (also used in the field), as it was the only power supply available at the start of the research period. The final filters were not connected at this stage (i.e. all samples shown are from point 3, at the output of the ioniser). Results are shown in Table 5.19. Run 1 is executed at a lower flow (Q = 0.5 Lpm), while Run 2 duplicates the flow, with other experimental conditions essentially the same. It can be observed that doubling the flow decreases the silver concentration by half in the first minute, showing a direct inverse proportionality. However, after running the experiment for 5 min a significant silver concentration drop is seen, down to 190 ppb.

In the second run, which was kept running for a longer period (30 min), silver is seen to apparently 'stabilise' at around 180 ppb, for Q = 1 Lpm (typical flow rate measured in the field). Interestingly, this value is only slightly lower to the silver concentration obtained for the first run. This could be due to higher ion concentrations accumulating at the ionising vessel during the first minute, subsequently being flushed and diluted with the new incoming water.

Table 5.19. Continuous flow ionisation: SilverLife power supply

Run	Flow (Lpm)	Time (min)	Ag (ppb)	Conduct. (μS/cm)
1a	0.5	1.0	390	130.0
1b	0.5	5.0	190	130.0
2a	1.0	1.0	190	130.0
2b	1.0	30.0	180	138.0

Note: Voltage ≈ 5V for all runs (switching period = 10 sec)
Cells in parallel to flow (CANG = 0)

Table 5.20 shows results for a continuous run using the Arduino power supply, which inverts polarities of the electrodes at pre-programmed times (15 sec in this case). A similar phenomenon to that of the previous experiment (Table 5.19) is observed here: silver starts at a higher value (at t = 1 min) and then decreases after 4 min. These concentrations are still sufficient for most bacterial disinfection purposes, and according to recommended guidelines (WHO 2008; Health and Safety Executive 2000; Landau 2007). The lower overall values are due to lower conductivities (the test was done on a different day to that above). Conductivity in the source RW varied according to the sampling period, as described in 3.3.2.1. Voltages are also slightly lower (4.8V), as these are fixed by the Arduino circuit and not user-controlled, as in the SilverLife unit or the fixed power supply. The nominal output is 5.0V (Voc) according to manufacturer specifications, but this drops after turning on the device and commencing the ionisation process (see 3.3.1.3). The linear effect of voltage and conductivity is discussed with greater detail in section 5.5.6.

Table 5.20. Continuous flow ionisation: Arduino 'switching' power supply

			Ioniser (3)		**Filters (4)**	
Run	Flow (Lpm)	Time (min)	Ag (ppb)	Conduct. (μS/cm)	Ag (ppb)	Conduct. (μS/cm)
3a	1.0	1.0	90	73.9	0	66.6
3b	1.0	4.0	60	73.9	10	66.6
3c	1.0	8.0	70	73.9	NA	NA

Note: Voltage = 4.79 V; Q = 1.0 LPM; Switching period = 15 sec. Cells parallel to flow

This run also incorporates the final 2-stage filter (Figure 3.14). The first sample (3a) shows a complete retention in the filter. A limited retention of metals is to be expected from GAC filters (Bitton 1994). However, as time progresses, some silver seems to be flushed through to the output, which can also be described as a saturation effect, as observed from the subsequent runs shown on Table 5.21. Here silver also drops to zero at point 4, after the filters, within 1 min of ionisation, but increases to a stable value of 60 ppb after 4 min. However, this still represents a significant reduction in silver concentrations (Figure 5.6).

Table 5.21. Continuous flow silver ionisation in Model I (Fixed power supply)

				Ioniser (3)		**Filters (4)**	
Run	Voltage (V)	Flow (Lpm)	Time (min)	Ag (ppb)	Conduct. (μS/cm)	Ag (ppb)	Conduct. (μS/cm)
4a	4.79	1.0	1.0	160	70.0	0	76.2
4b	4.79	1.0	4.0	190	70.0	60	68.6
4c	4.79	1.0	8.0	190	70.0	60	76.2
5	5.08	0.6	1.0	330	82.4	NA	NA
6	4.87	1.0	4.0	200	90.0	40	90.0

The tests in Table 5.21 were performed with a fixed power supply. Significantly higher silver concentrations were obtained compared to using the Arduino, for similar conductivities and sampling times, as shown on Figure 5.5 (compare samples 4a – 4c with the values in Table 5.20). Since this test was set up specifically for this purpose, voltage in the fixed power supply was set exactly to 4.79V, the operating voltage produced by the Arduino circuit. Both sets of runs were also done on the same day, to ensure similar test water conditions. The effect of fixed vs. 'switching' power supplies is further analysed in section 5.4.5.

Table 5.21 also contains two additional runs. The first one (5) confirms the effect of reducing the flow by roughly 40%, with an important increase in silver concentration

from 160 (4a) to 330 ppb, similar to the case noted above in Table 5.19. This corresponds to approximately double of the original value, although it must be noted that voltage and conductivity are slightly higher for this test, though not enough to account for such a substantial increase in silver ion generation. The next run (6) is an attempt to repeat Run 4a (same flow and sampling time), though the voltage was exactly the same (0.1 V difference), and the conductivity was higher in this case, a similar silver value was obtained in point 3 after 4 min of ionisation. The 10 ppb increase (from 190 ppb in the first run to 200) could be due to the variation in conductivity, or to the fact that in this particular run the cell angle was unintentionally placed at 90º (perpendicular to the flow), instead of in parallel, as in all the other runs (see 5.5.6.3). In conclusion, it seems like a 'stable' concentration is reached after a few minutes of constant flow in all the cases described.

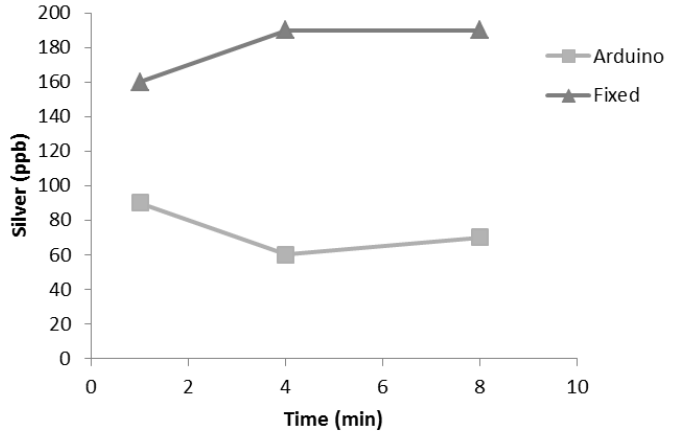

Figure 5.5. Comparison of fixed and 'switching' power supply

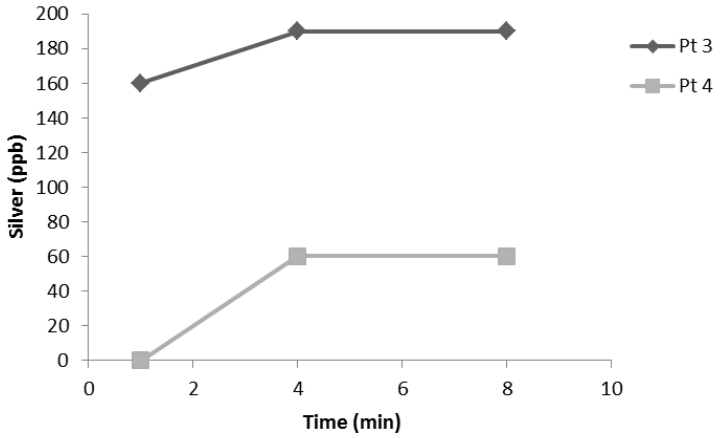

Figure 5.6. Silver reduction by filters in continuous flow (Q=1 Lpm) with fixed voltage

5.2.2 MODEL II

This tubular model (without filtration or pumping) is described in 3.3.3.2. The model was tested first using tap water and then RW, for comparison across two different conductivity ranges. Sampling points below refer to those indicated on Figure 3.15).

For all the tests listed in this section the SilverLife power supply was used (3.3.1.3), with a polarity switching time between the two electrodes of approximately 10 sec. Flow occurred naturally, by pulling down water from the feeder tank as sampling valves were opened for analysing. This 'flow' was estimated to be 0.2 – 0.4 Lpm.

5.2.2.1 Tap Water

Once the model had been filled with tap water, according to the described procedure, an experiment was started with the following initial conditions:

Voltage = 5.0 V
Ionisation time = 5.1 min
Conductivity = 692 μS/cm
pH = 8.1
Turbidity = 0.4 NTU (at all points)
CANG = 90 (perpendicular to flow)[25]

Results are shown in Table 5.22. Conductivity and pH were not seen to vary significantly during the experiment. For instance, in the actual ionising vessel, after concluding the experiment (where presumably silver concentration was the highest), conductivity was measured to be 658 μS/cm, even lower than the original reading of 692 μS/cm. The reduction in turbidity values as silver particles gradually precipitate out of solution can be observed in Figure 5.7. On the first day, right after ionisation, the highest turbidities were observed next to the ioniser (point 2), where presumably silver particles will be more abundant, and then dropped sharply in the more distant sampling points.

Turbidity was also found to be high (358 NTU) after stirring up the sediment deposited at the bottom during ionisation, which was only done after the experiment had concluded. This shows that the silver precipitate can account for the increased turbidity.

[25] This is an SPSS variable, defined as the angle of the silver cells/coins to the incoming water flow. It is reported here since it was later observed to have an effect on silver generated (5.5.6.3).

Table 5.22. Turbidity and silver ion diffusion in Model II using tap water

	DAY 1		DAY 4		DAY 5	
Sampling point	Turb (NTU)	Ag (ppb)	Turb (NTU)	Ag (ppb)	Turb (NTU)	Ag (ppb)
Feeder tank (1)	0.4	0	0.4	0	NA	NA
Ioniser (2)	56	[1] 830	3.9	110	2.8	[3] 50
Cylinder (3)	[2] 23	NA	3.8	NA	[4] NA	NA
Final effluent (4)	2.6	NA	3.2	NA	2.2	50

1. Reading repeated (from stored sample) on Day 4: Ag=770ppb; 36.0 NTU
2. Turbidity reading was repeated from stored sample (without stirring) on Day 4: 13.2 NTU
3. Taken as estimate and not accurate reading, as silver reagents had recently expired
4. Sample not measured but presumed to be between 2.2 and 2.8 NTU (points 2 and 4)

Samples were taken 3 and 4 days after ionisation directly from the model's sampling points in order to test the behaviour of silver ions and turbidity over time. Some samples were stored in sealed plastic bottles and retested at a later date (see footnotes of Table 5.22). Silver was measured in the lab using spectrophotometry, and be seen to have a limited diffusion through the pipe, even without flow. The fact that silver precipitates out of the solution within a few days in tap water (faster than in lower conductivity RW), was also confirmed experimentally in batch tests (section 5.1.6). A clear correlation can also be observed between turbidity and silver concentrations (Figure 5.8), despite the small number of samples available.

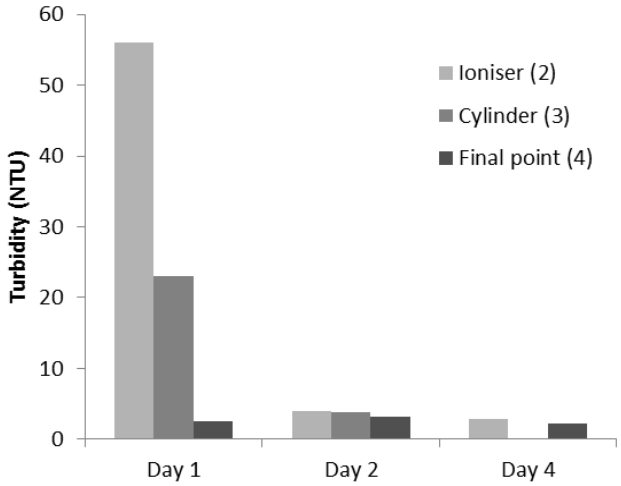

Figure 5.7. Turbidity reduction with time throughout the different sampling points

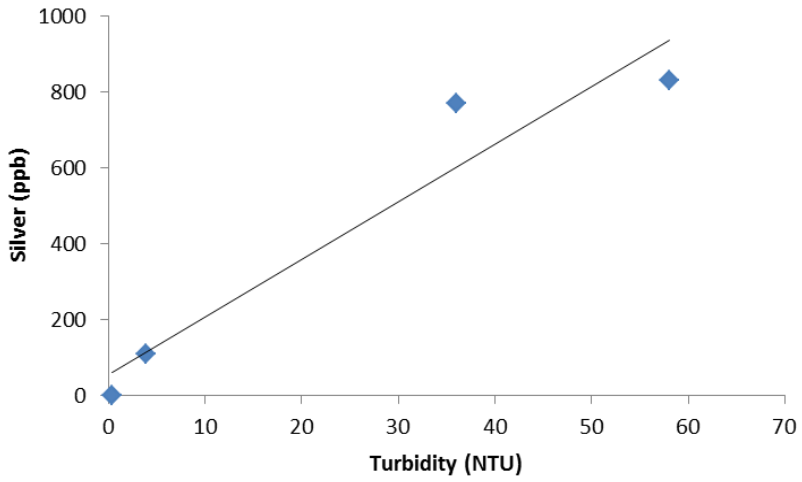

Figure 5.8. Relation between selected turbidity and silver measurements

5.2.2.2 Rainwater (RW)

After flushing and rinsing thoroughly, to eliminate trace residuals from the previous experiment, the model was entirely filled with rainwater, according to the methodology described in 3.3.3.2. The following test conditions were set up:

Voltage = 5.1 V
Ionisation time = 5.0 min
Conductivity = 117 μS/cm (TDS = 52.0 mg/L)
pH = 7.2
Turbidity = 4.9 NTU (at all points)
CANG (cell angle) = 0 (parallel to flow)

Main results are shown in Table 5.23. Silver is seen to drop after the ioniser point from 770 to 690 ppb after one day. Again, a significant turbidity increase is observed where silver is the highest, from an initial 4.9 NTU to 35 NTU, though the level reached (of both silver and turbidity) is lower than for tap water (Figure 5.9), as expected. The comparison can be done since same voltage and ionisation time was used in both tests.

The silver ion decay after a day is seen to be considerably slower in RW compared to tap water (5.1.6). Another phenomenon observed in this experiment is the migration of silver ions to the feeder tank (point 1) on the second day, confirming that the ions are able to diffuse 'upwards' in RW (against gravity) under stagnant conditions, in sharp contrast to tap water, where no silver was found in point 1 on any of the samples (Table 5.22).

Table 5.23. Turbidity and silver ion diffusion in Model II using RW

	DAY 1		DAY 2	
Sampling point	Turb (NTU)	Ag (ppb)	Turb (NTU)	Ag (ppb)
Feeder tank (1)	4.9	0	6.4	[1] 20
Ioniser (2)	35.0	770	NA	690
Cylinder (3)	5.3	NA	NA	NA
Final effluent (4)	5.0	NA	4.9	NA

1. This sample was also analysed using ICP-MS obtaining 26.8 ppb.
Hach spectrophotometer result reported here for ease of comparison

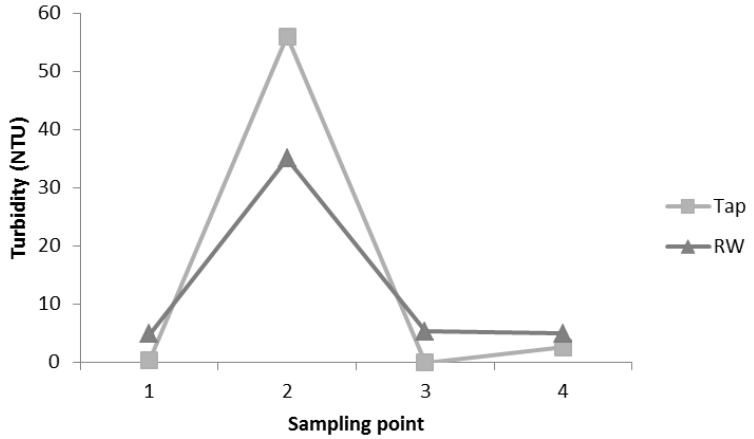

Figure 5.9. Turbidity comparisons in Model II along sampling points (Day 1)

5.2.3 MODEL III

As described in the methodology (3.3.3.3), this model was used mainly for controlled gravity flow ionisation tests as well as a bacteriological experiment. Flow was regulated by opening the valve on sampling point 2 (Figure 3.16), measured using a cylinder and stopwatch, as no flow meter was installed in this model.

5.2.3.1 Silver ion release

Table 5.24shows the results of selected ionisation experiments using this model. The same batch of rainwater was used for all tests, ensuring similar water quality conditions (Conductivity ≈ 140 µS/cm; pH = 7.4). A fixed polarity power supply was applied to the silver cells of the full-cell device. Electric current (I) was monitored for the first time during the research process and is also reported here, along with the cell angle of the device (CANG), which was seen to have an effect in silver generation

(Section 5.5.6.3). More current variation experiments using this model are summarised in the corresponding section on electric parameters (section 5.4).

Table 5.24. Gravity flow experiments: Point 2 measurements (outflow)

Voltage (V)	Flow (Lpm)	Time (min)	Ag (ppb)	CANG (degree)	I (mA)
5.06	0.2	1.0	[1]920	[2] 90	5.95
5.06	0.3	0.8	670	0	6.09
5.04	0.6	1.0	290	0	6.00

1. Value above linear range of instrument, reported here as a best approximation
2. 90° refers to cells perpendicular to the incoming water flow, with the anode (+) cell first

As was observed with Model I (section 5.2.1), flow seems to be inversely related to silver generation, since all 3 runs have very similar voltages and sampling times. The third run, for instance, produces 290 ppb of silver with a Q =0.6 Lpm, while reducing this flow by half, generates approximately double the amount of silver. The first line of Table 5.24, however, highlights a special case. Even though a slight silver increase would be expected, following the same logic, by reducing the flow from 0.3 to 0.2 Lpm, the considerable increase is probably due to the cells being in parallel, which would increase retention time, particularly for low flows (see 5.5.6.3 for a discussion on this issue).

Silver was not found in any of the point 1 samples (Figure 3.16) during continuous flow operation. To test for 'backwards' diffusion, power was applied (at 5.0V) using the same fixed polarity supply for 6.5 min, but without flow. The height of the feeder tank (beaker) was also decreased from 40 to 20 cm, allowing for a better diffusion. After 1 hour, Ag was measured to be 680 ppb at the ioniser output (point 2), but was still zero in the feeder tank, showing that there was no 'backflow' of ions upstream through the rubber tube, in this case, against gravity. It could have been that with a longer period of time, some diffusion would have been observed, as was seen in Model II (5.2.2.2).

5.2.3.2 Microbiological removal

The model was run using RW, with an approximate gravity flow of 0.5 – 0.6 Lpm and a fixed voltage on the full-cell device of 5.04V. Inoculation onto the feeder tank (beaker) then took place using a pre-tested batch of WG-5 *E. coli*, adding 0.5 ml of a concentrated stock solution (see methodology notes on 3.3.5.2) into 1 L of RW, mixing and dosing it into the model slowly via the feeder tank (at constant flow). Results are shown in Table 5.25. Samples were analysed by duplicate, showing similar results (zero colonies after the ioniser and TNC in the inoculated sample).

Table 5.25. Disinfection efficiency in RW using Model III

Sampling Point	Ag (ppb)	*E. coli* (CFU/100 ml)
Before ioniser	0	1200
After ioniser	290	0

Notes: Bacterial analyses were done using Millipore Coliblue broth.
Cells were parallel to the flow (CANG=0)

The results show that a complete elimination of the bacterial indicator (1,200 CFU/100ml) was achieved in less than 1 min of running through the model. Since this concentration is in the highest range of total coliform counts seen in the field (4.2.3), it can indicate a satisfactory efficiency for most practical situations herein described. The silver concentration generated is also sufficient for the inhibition of the highly resistant viral indicators (bacteriophages), according to the preliminary experiments detailed in the following section.

5.3 BACTERIOPHAGE TESTS

Results for some of the bacteriophage tests described below were published and presented at an IWA conference in Korea (Adler et al. 2012).

5.3.1 PHAGE PRESENCE IN NATURAL WATERS

To test the methodology (described in 3.3.5.3) as well as to obtain strains for culturing, two samples from surface waters were taken (Thames River and Regent's Park Lake) and analysed for bacteriophages, using 1 ml of sample on each occasion, as suggested in the literature (Martha R. J. & Kropinski 2009). Duplicate samples were also analysed. Numerous plaque forming units were found in each case (TNC), confirming the correct methodology. However, no colonies were found in the rainwater barrel, even after increasing sample size to 10 ml (from normal 1 ml), using the largest available petri dishes (15 cm). The experimental composition used for both analyses is shown on Table 5.26.

Table 5.26. Sample composition for bacteriophage testing

	Surface water	**Rainwater**
Sample size (ml)	1	10
MSAss[1] (ml)	2.5	25
WG-5 *E. Coli* host (ml)	1	1

1. Modified Scholten's semi-solid agar

5.3.2 INITIAL RESPONSE TESTS

For the following experiments, a silver stock solution was electrolytically prepared by applying 5.0 Volts to the 'floating' half-cell device, partially submersed in sterile deionised water. This solution was stored in a clear plastic bottle and conserved in the dark at ambient temperature. Total silver was measured initially to be 600 ppb using spectrophotometry, and was then checked regularly, with the concentration remaining relatively constant throughout the course of the experiments. This solution was labelled Ag600 accordingly, as shown in the following tables.

Table 5.27 shows the composition of each experimental sample, including blanks. To keep results consistent, a fixed amount of phage was added to each sample: 50 µl from the prepared titre described above. Total sample volumes were also kept constant at 30 ml. The mixture of rainwater, coliphages and silver ions was continually shaken gently (using a shaking plate at low speed) to ensure an adequate and even interaction. Reaction time was approximately 25 min. Rainwater was obtained directly from the water butt without any filtration or pre-treatment. Inoculation was done by directly pipetting into the mix from a vial of prepared phage titre at an initial concentration of 10^6 pfu/ml (see 3.3.5.3).

Table 5.27. Phage response to lower silver concentrations

Sample	**Composition**	**Silver** (ppb)[1]	**Phage counts** (pfu/ml)[2]
1	30ml RW + phage	0	58
2	20ml RW + 10mL DI + phage	0	250
3	10ml Ag600 [3] + 20ml RW + phage	200	0
4	30ml RW + 30uL Ag Std[4] + phage	820	0

1. Measured with Spectrophotometer. Zero values to be interpreted as 'below detection limit'
2. Phage counts shown represent the average of duplicate samples
3. Ag600 refers to the electrolytically prepared solution described above (Ag=600 ppb)
4. 'Std' refers to pure Jenway Silver Standard (1,000 mg/l)

Samples 1 and 2 in the table above are experimental blanks. The reason for doing two of them was to make sure that the dilution of rainwater with deionised water, in the same proportion as in sample 3, was not having a detrimental effect on phage growth (since the silver solution is prepared on a DI base). However, it can be observed from the results that counts were actually higher than in the pure rainwater. This does not necessarily mean that bacteriophages grow better in the diluted water, since a number of random conditions can influence the growth of a microorganism, even under

controlled conditions such as these. Such an effect would need to be proved with repeated statistical experiments, beyond the scope of the current work. It suffices to know that there wasn't any particular inhibitory condition, allowing results to be expressed with greater confidence.

It was observed with this initial experiment that a total elimination of the viral indicator occurred, even in the lower silver concentration applied (200 ppb). A follow-up experiment was performed using a lower concentration (Table 5.28), prepared by diluting the same stock solution in a higher volume of rainwater. In this case, the amount of phage titre added was increased to 500µL in order to maintain the same proportion as in the previous experiment.

Table 5.28. Phage response to lower silver concentrations

Sample composition	**Silver** (ppb)	**Phages** [pfu/ml] (5 min)	**Phages** [pfu/ml] (20 min)
300ml RW + phage (blank)	0	270	660
300ml RW+100mL Ag600+phage	140	50	24

The additional parameter of reaction time was added to this experiment, collecting samples at 5 and 20 minutes respectively (times given are approximate). As can be observed, the starting phage concentration is similar to the previous case (270 pfu/ml). However, it increases sharply after 20 min. The sample treated with silver, on the other hand, shows the inverse behaviour, with an initial decrease in phage counts of roughly 81%, followed by an elimination equivalent to about 96% in the second point (Figure 5.10).

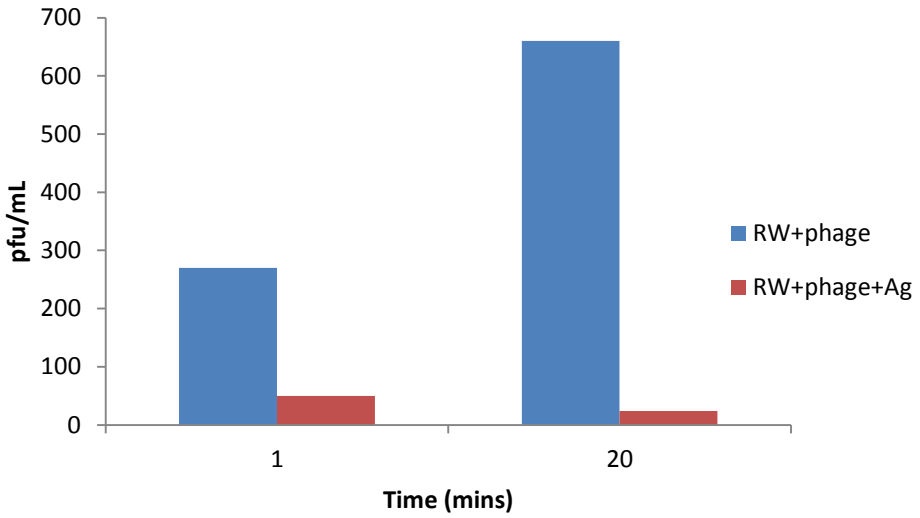

Figure 5.10. Bacteriophage removal in rainwater at Ag = 140 ppb

It is worthy of notice that there is not a total phage elimination with this lower concentration, which might lead to the conclusion that the silver concentration 'threshold' for complete phage elimination would be between 150 and 200 ppb, given the reaction time and conditions used. However, repeated experiments with a wider control of potentially interfering variables would be needed in order to fully assert this.

5.3.3 EFFECT OF SILVER ADDITION ON HOST BACTERIA

Another factor to be considered is the issue of neutralization. Since silver purportedly has a bactericidal effect, it could well be that free Ag+ ions would inactivate the host bacteria, a susceptible *E. coli* strain, rendering the test useless. Many authors resort to the use of neutralizers such as sodium thiosulfate (Butkus et al. 2005; Kim et al. 2008) in order to stop the disinfection process at predetermined times. However, in this case it was observed that the semi-solid Modified Scholtens' Agar (MSAss) in which the samples must be immersed before plating, according to the method used (BS EN ISO 10705 2001), acts as a powerful neutralizer, due to its high concentration of anions that react or precipitate the silver cations.

This statement was tested by adding 10 ml of a 100 ppb Ag solution (prepared from silver standard and diluted in DI) to 40 ml of Modified Scholtens' Broth (MSB), using the same standard procedure cited above. This was equivalent to a 1:5 dilution of the original sample in the broth, which is close to what would be done in a regular coliphage test, according to the prescribed method. The diluted silver solution was measured using spectrophotometry immediately upon addition and was noticed to drop down to 0.0 mg/l. The possible interference of colour or high nutrient content from the broth was not taken into account. Given that the experiments showed consistent results, without any noticeable elimination of the bacterial host, this neutralization on behalf of the broth was deemed sufficient for the present tests.

Furthermore, the addition of sodium thiosulfate could have interfering bactericidal or virucidal effects of its own that have not been fully determined.

To test the effect of the silver solution on the host bacteria, as well as to validate its disinfection capacity, an experiment was performed where 4 different silver concentrations, prepared by diluting in deionised water the original Ag600 solution (see previous section), were added to a fixed stock of *E. coli* (WG-5 strain), which is the same used for the bacteriophage experiments described above. This strain is known to be resistant to Nalidixic Acid (an antibiotic), and can thus be considered a good indicator of bacterial disinfection for other common strains. The bacteria were left to react in 1 ml sterile Eppendorf vials for 20 minutes before plating on a Modified Scholtens Agar plate (MSA). This was prepared according to BS EN ISO 10705 (2001), using the same procedure as for bacteriophage tests. For the sake of comparison, a duplicate test was performed on Tryptic Soy Agar (TSA), which is a more common growth media.

Table 5.29. Bacterial elimination with selected Ag concentrations

	E. Coli counts (CFU/ml)	
Ag (ppb)	TSA	MSA
Control	2.0×10^4	2.2×10^4
50	1.0×10^4	0
140	0	0
300	0	0
600	0	0

Bacterial counts were done using the Miles & Misra method (Miles et al. 1938). As shown on Table 5.29 above, bacterial elimination was complete even at the lowest concentrations used, proving that viral bacteriophages are indeed more resistant than traditional bacterial indicators.

It is noteworthy that even though there was a 100% reduction at 50 ppb Ag using the MSA broth, only a halving of the initial concentration was observed in TSA media, which tends to have a wider, less specific growth spectrum than MSA, specifically used for the bacteriophage host. At silver concentrations above 50 ppb, including the lowest one used for the phage removal tests described in Table 5.28 (140 ppb), elimination was complete in both types of media.

5.3.4 SUMMARY

The results obtained show that there is an important reduction of somatic coliphage levels upon exposure to silver in rainwater. This is encouraging, given that viruses in general tend to be more resistant to traditional disinfection than bacteria (Baggi et al., 2001). One of the challenges posed by the methodology is the vulnerability of the *E. coli* host to the residual silver ions. It was shown by repeated assessments, however,

that the rich nutrient broth in which the host is grown acted as a powerful silver neutralizer, which precipitated upon reaction with the negatively charged anions. The neutralisation of silver by different agar media has been explored in greater detail by Tilton & Rosenberg (1978).

Bacterial test results were in agreement with those presented in the field studies (see Ch. 4), achieving complete elimination with relatively low silver concentrations (<100 ppb). Consistent with the literature, the silver concentration threshold for complete phage elimination seems to be somewhat higher (Butkus et al. 2005; Kim et al. 2008). Reaction time, however, is an important factor to be considered in further studies, as well as other variables, such as temperature and pH, which should be closely monitored.

5.4 ELECTRIC CURRENT

Ultimately, it is the electrical current that will determine how much silver (or any other metal being dissolved, for that matter) will be released into a liquid solution (see 5.5.6.1). A series of experiments was thus performed to determine the effect of a number of parameters on electric current (i.e. conductivity, voltage, distance between electrodes, volume of silver cell immersed in water).

In contrast to a standard wire or solid conductor, where electrons on the outer layer will displace electric charge from one atom to the other, in a liquid medium electric energy will be transmitted by the movement of charged ions ((Benjamin 2002)). Notwithstanding, the same basic principles of electricity apply, namely Ohm's Law, which states the electric current generated in a medium is directly proportional to the voltage applied, and inversely proportional to the electric resistance of the conductor:

$$\boldsymbol{I = \frac{V}{R}} \qquad [5.2]$$

Where I (current) is in Amps and V in Volts. In the case of water, the resistance (Ohms) will be inversely proportional to the conductivity. The conductivity of drinking water tends to be low (i.e. high resistance), with units in the order of μS/cm being the norm (Benjamin 2002).

5.4.1 PERFORMANCE ACCORDING TO IONISATION DEVICE

The results below summarise some of the current measurements performed for the silver ionisation experiments described above, as well as additional tests done specifically for variations of current and electric parameters. Due to the large number of runs, only relevant statistical summaries are presented here (Table 5.30 to 5.32), where N represents the number of samples and M the mean.

Table 5.30. Electric measurements using the half-cell device

Water Type	N	Current (mA)		Voltage (V)		Conduct. (µS/cm)		pH	
		M	Range	M	Range	M	Range	M	Range
DI	5	0.11	0.09 - 0.15	5.04	5.03 - 5.06	2.0	2.0 – 2.0	5.9	5.6 - 6.2
RW	4	2.09	1.24 - 2.4	4.93	4.8 - 5.04	107.9	79 - 120	6.5	6.5 - 6.5
TAP	6	15.23	9.7 - 21.6	7.27	4.97 - 9.54	645.2	635 - 658	7.9	7.9 - 7.9

Table 5.31. Electric measurements using the full-cell device

Water Type	N	Current (mA)		Voltage (V)		Conduct. (µS/cm)		pH	
		M	Range	M	Range	M	Range	M	Range
RW	23	4.70	3.41 - 17	5.07	4.79 - 9.94	83.4	60 - 130	6.8	6.4 - 7.3
TAP	2	42.00	25 - 59	7.32	5.1 - 9.54	658.0	658 - 658	7.9	7.9 - 7.9

Table 5.32. Electric measurements using silver rods

Water Type	N	Current (mA)		Voltage (V)		Conduct. (µS/cm)		pH	
		M	Range	M	Range	M	Range	M	Range
DI	3	0.04	0.02 - 0.07	10.00	5 - 20	1.5	1.5 - 1.5	NA	-
RW	23	1.88	0.15 - 8.7	6.33	4.81 - 20	98.7	79 - 120	6.5	6.5 - 6.5

5.4.1.1 Comparison across devices

If we select from the data only those cases where the Voltage is approximately 5V (the most common setting and the one generally used in the field), as well as 'fixed' power supplies, in order to discount for current fluctuations that arise with switching polarities (see section 5.4.5), then a reasonable comparison can be drawn between all 3 devices for each water type. The selected data is shown on Table 5.33. For silver rod measurements, only those with standard water submersion values (HSUB=5 cm) are displayed, in order to reduce variability which could lead to erroneous conclusions.

Table 5.33. Current performance comparison in RW across devices (similar voltages)

Device	**N**	**Current (mA)**		**Voltage (V)**		**Conduct. (µS/cm)**	
		M	Range	M	Range	M	Range
Half-cell	3	1.98	1.24 - 2.4	4.95	4.8 - 5.04	106.3	79 - 120
Full-cell	16	4.17	3.4 1 - 6.09	4.85	4.79 - 5.06	82.8	68.5 - 130
Rods	8	1.38	1.00 - 2.08	4.86	4.81 - 5	84.2	79 - 120

An important issue that arises in drawing such a comparison is that conductivity is prone to variation within the same test water group (see Annex A). A simple analysis based on the summary data of Table 5.33 shows this to be the case[26], particularly for the half-cell device samples, and thus an ideal comparison cannot be made due to the expected variation of current with conductivity.

However, important conclusions can still be drawn from this data. As shown in Figure 5.11, current values for the full-cell device are considerably higher than that for the half-cell device, *despite* there being a significantly lower conductivity in the former case. In other words, should conductivities have been exactly the same throughout all tests, in an ideal scenario (as this variable was not controlled experimentally), current output for the full-cell device would have been comparatively *higher*, given Ohm's law (Equation 5.2).

The silver rods had considerable variability in the distances between them, among other factors, and comparisons cannot objectively be done. However, in general terms the current generated by the rods seems lower that with the other devices, which would be a reasonable assumption given the smaller total volume and surface area. Figure 5.11 shows average current and conductivity for each device.

[26] Levene's F-test statistic reveals that variances are in fact not homogenous ($p<0.05$)

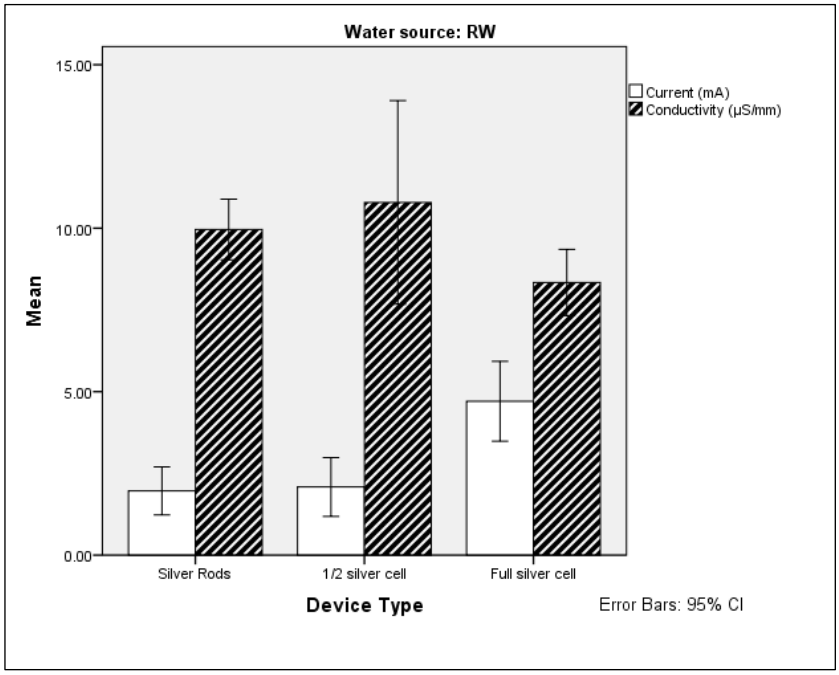

Figure 5.11. Current and conductivity according to ionisation device[27]

5.4.2 CURRENT INCREASE OVER TIME

As ionisation occurs in a fixed volume of water, the added presence of charged particles will increase the conductivity and thus the current flowing through the electrodes. It has been noted elsewhere in this report that measured conductivities did not vary significantly with ionisation times in natural waters (i.e. RW and tap water). This is, however, more likely due to the fact that changes are relative (i.e. effect being noticed only when the starting value is small enough), or to issues related to lab meter resolution and to the measurement process itself. For instance, as discussed in Section 5.5.1, conductivity showed a noticeable increase in several readings during ionisation in DI, where there are little or no free ions to interact with the charged silver particles which are being released.

The following experiment, summarised in Table 5.34, shows the small increases that occur over the course of a few minutes of ionisation. The test was performed with silver rods (described in 3.3.1.2), immersed in a glass beaker with 700 ml of RW, at

[27] Error bars represent 95% confidence intervals. Note that conductivity unit was changed to µS/mm for better graphical comparison.

an approximate distance (d) of 9 cm. Voltage was kept constant at 5.0V (using a 'fixed polarity' DC power supply). Current readings were done by setting the multimeter to the 'μA' scale to get a more accurate precision. RW conductivity was measured to be 120 μS/cm.

Table 5.34. Increase of current over time in RW

Time (min)	**V** (volts)	**I** (μA)	**Rate** (μA/min)
0	5.0	1125	-
1	5.0	1137	12
2	5.0	1145	8
3	5.0	1146	1
4	5.0	1149	3
10	5.0	1190	*

* Current stabilises, increasing at a much slower pace (not measured)

It can be observed that the rate of current increase seems to drop over time, stabilising at a value of 1190 μA, and rising very slowly thereafter. The positively charged silver ions will repel each other as more are released into the water, tending to 'slow down' the current carrying capacity of the newly released ions. This rate of change, however, does not behave in a strictly exponential fashion, but displays irregular variations, though always on the rise (Figure 5.12). These fluctuations could be due to a number of factors, including low resolution of the instrument and external electromagnetic interference or 'noise'.

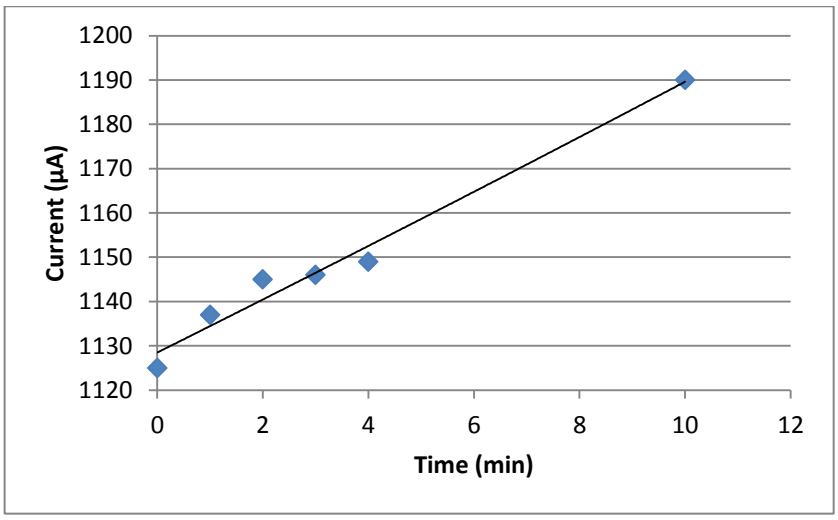

Figure 5.12. Scatter plot (with trendline) of current increase vs ionisation time

A similar test was performed using the full-cell device, with a higher voltage (9.94 V). The ionising vessel (of approx. 300 ml) was filled with water for this purpose. In this case current steadily increased from 14 mA up to 17 mA in approximately 1 minute, with the following parameters: Conductivity = 119 µS/cm; pH = 7.2.

5.4.3 Effect of Flow

An unexpected result from these operational tests was the fact that water flow (Q) had a positive effect on electric current. The experimental detailed in Table 5.35 shows a marked current variation of close to 1 mA, as the flow increases from 0 to approximately 1.5 Lpm (Figure 5.13). The test was performed using RW (Conductivity ≈ 70 µS/cm) on the continuous flow model described in 3.3.3.1. Voltage was fixed at 4.80V, with the cells perpendicular to the flow (CANG = 90º). As soon as the pump was turned off, stopping all flow, the current instantly dropped back to approximately the starting value (I = 3.42 mA).

Table 5.35. Q vs I variations

Q (Lpm)	**I (mA)**
0.0	3.43
0.3	3.70
1.0	4.01
1.4	4.24
1.5	4.30

There is scant information in the literature about this phenomenon. A plausible explanation is that the water flow agitates settled particles throughout the system which then increase the total dissolved solids (TDS) content, thus making the electric current between the cells rise. The simple experiment described in the following section (5.4.4) seems to validate this, though there could be a number of reasons which would need to be investigated in further detail.

The benefits of this current variation are self-evident. The more water is flowing through a purification system, the greater the demand for silver (or copper) ions. In fact, many manufacturers and patent-holders have designed methods to automatically regulate current proportionally to the flow, in order to maintain a stable and consistent ion concentration in the system (Tarn-Pure 2013; AquaLyse 2013). One such system adapts the flow rate to the resistance (i.e. conductivity) of the water being treated (Henson 1984).

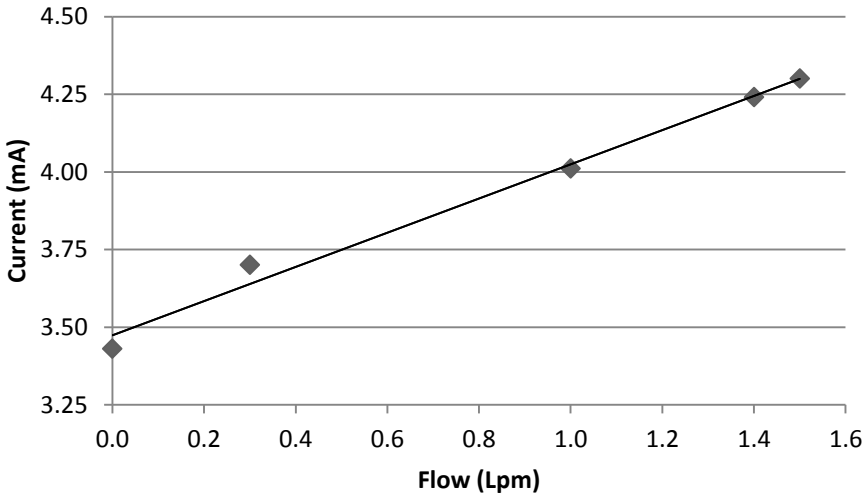

Figure 5.13. Scatter plot of current vs flow, including trendline (slope = 0.55)

5.4.4 EFFECT OF WATER VOLUME/CONTAINER

To ensure that ionisation current was unaffected by the total water volume, or the dimension of the container used in the laboratory, the experiment detailed in Table 5.36 was carried out. Different volumes of RW from the same source were poured into two entirely different containers, as shown below. Silver rods (3.3.1.2) were inserted at fixed water depths.

Table 5.36. Electric current variations in different containers

Container	**Dimensions (cm)**	**Volume (ml)**[1]	**I (mA)**	**Conductivity (µS/cm)**	**pH**	**TDS**[2] **(mg/l)**
Beaker (1 L)	9.6 (diam.) x 12.2 (height)	860	1.09	79.0	6.5	36.1
Plastic Box	23 x 15.5 x 7.8 (height)	2780	1.14	82.4	6.4	37.6

1. Volumes are estimated from container dimensions and water height
2. Total Dissolved Solids, measured with Mettler-Toledo meter, same as conductivity

Currents were measured and compared using a multimeter. When switching back and forth between the containers, variation from these values was minimal. Experimental conditions were carefully kept constant for both containers, with the following characteristics:

- Temperature = 27.7 C
- Voltage = 4.82 V (measured directly on silver cells)
- Power supply: Fixed polarity
- Submersion of rods in water (HSUB) = 5 cm

The water in the plastic 'box' (which was basically a large Tupper) looked slightly more turbid, with small floating particles, which could account for the small difference in TDS (and thus current). When this water was stirred, the current was seen to increase, possibly due to the agitation of particles, up to approximately 1.25 mA, with the meter displaying variable readings. As the particles settled, within a few minutes, the current progressively dropped back to 1.12 mA (close to the original value) and the meter stabilised. This test was repeated a number of times with the same general result: a current increase with greater stirring.

5.4.5 EFFECT OF POWER SUPPLY

As described in the methodology (3.3.1.3), different electric power supplies were used to operate the silver ionisation process. Since this research project is mainly concerned with the practical applicability of the technology in the field, this is a highly relevant matter. The power sources used for the laboratory experiments can be classified as follows:

a) Fixed (i.e. without 'switching' or inverting polarity on the silver cells)

- Regulated power supplies (0 – 10V and 0 – 15V)
- Standard household battery (9V)

b) Switching (inverting polarity on the cells automatically on a set period)

- SilverLife: Original power supply installed in the field. Voltage is variable from 0 – 15V (approx.), with a constant factory-set switching period of 10 – 11 seconds.
- Arduino: custom-made microprocessor programmed and assembled specifically for this project, with a variable user-adjustable period of up to 15 seconds (Figure 3.12) and a rated output voltage of 5 V (actual measured value was 4.97 V).

An experiment was performed to investigate whether using different power supplies would make any difference on the current supplied to the cells, which as described in Section 4.1 is the key factor that determines the amount of silver ions released. The half-cell device was inserted into a glass beaker with 800 ml of tap water. Using the regulated power supplies listed above, voltage was adjusted to 9.5 V, as this was the precise voltage measured on the battery. In this manner, three 'fixed' supplies were set to exactly the same electric potential. Then the connection was made to the device for each one of them and current monitored using a multimeter.

Table 5.37. V-I measurements using fixed power supplies

Voltage (V)	**Current** (mA)	**Conductivity** (µS/cm)
9.5	21	635
5.0	10.1	665

Note: pH was measured to be 7.9 in both cases

Results are summarised in Table 5.37. When the voltage on the two regulated supplies was lowered to 5.0 V, the current was measured again and determined to be identical in both cases. In other words, the power supply used is not relevant to the ionisation process as long as it has the capacity to deliver the required amperage. Current is also seen to vary linearly with voltage, which is expected according to Ohm's law (equation 5.2). As a side-note, resistance was measured directly (by inserting the meter tips into the water surface), and determined to be roughly 30 KΩ, at a distance of 1.5 cm, though this was highly variable and should not be taken as a substitute for conductivity measurements.

5.4.5.1 Peak currents

An entirely different matter occurred when attempting to compare 'switching' with 'fixed' power supplies. This has to do with the polar nature of water molecules, which will orient themselves in the direction of an external electric field, acquiring a partial charge (Kegley & Andrews 1998). This was measured by directly inserting the voltage meter tips into the water as ionisation was taking place. Different electric potentials could be detected (always lower than the actual voltage applied to the cells) depending on where in the water surface the water measurement was made. The closer to the silver cells, the higher the reading. Since water is behaving as an electric conductor, this should not come as a surprising result.

The more relevant phenomenon occurred when the power supply was disconnected. Voltage was seen to remain for 30 – 60 seconds on the water surface, decreasing gradually, indicating that the water molecules are staying polarised, even after the power supply has been switched off. The insulation properties of water make the liquid in between the cells behave much in the same way as an electric capacitor, storing charge temporarily. Thus, when polarity on the electrodes is suddenly reversed, a certain degree of resistance would be expected, as the molecules need to be realigned with the new electric field direction.

The practical implications for this were observed throughout several tests, where a peak current was observed at the time of switching polarities (or when turning on the power supply for the first time), taking several seconds to stabilise (Table 5.38). This behaviour is similar to the 'surge' that occurs in an electrical engine when turned on or reversing directions, since an inertia needs to be overcome, causing more power to flow through the wires until conditions are stabilised. In the case of water, the realigning of the polar molecules creates a higher energy demand, until the new electrical pathway has been formed and current can flow smoothly.

Table 5.38. Peak currents in RW using different devices (data selection)

Device	Voltage (V)	I (mA)	Ipeak (mA)	Stabilisation time (sec)[1]	Conductivity (µS/cm)
I	4.80	1.24	1.50	60	79.0
II	4.87	4.00	5.11	90	90.0
Rods	4.96	2.08	2.67	80	79.5

1. Stabilisation times (given in seconds) are approximate

5.4.5.2 Effect of polarity inversion

The main purpose behind inverting polarity, is to prevent scaling from forming on the electrodes and to avoid one from wearing away more than the other, promoting a symmetrical degradation of the silver cells (Landau 2007). Particularly in hard waters, salts can become attached to the electrodes, though less so in RW (see Section 5.5.2). The formation of scale on one any of the electrodes will increase power consumption while reducing the amount of silver released into the water.

The following experiment compares both a 'fixed' and a 'switching' power supply, under identical conditions. A volume of 800 ml of RW was poured into a glass beaker. Silver rods were inserted at a fixed submersion depth (HSUB) of 5.5 cm (approx.) separated by a distance (d) of 2.5 cm. Ionisation was performed at a constant voltage of 5.0 V for approximately 4 minutes, using first the 'fixed' regulated power supply and then the Arduino 'switching' power supply described above, set to a period of 15 seconds. Between samples the container was thoroughly rinsed, using a new batch of RW at the same volume. Since the water came from the same source,

parameters remained basically constant in both tests (pH = 6.5, Temp = 27.5ºC. Conduct. ≈ 80 μS/cm). Results are shown on Table 5.39.

Table 5.39. Effect of power supply on silver ionisation

Power supply	**Voltage (V)** [1]	**Ipeak (mA)** [2]	**I (mA)**	**Silver (ppb)**	**Ionisation time (sec)**	**Conductivity (μS/cm)**
Fixed	4.96	2.67	2.08	650	240	80.3
Arduino	4.91	3.16	1.71	230	270	80.7

1. Measured directly at the silver cells. Voltage on power supplies was slightly higher
2. Stabilisation time for the fixed power supply was 80 sec.

It can be clearly observed that the silver concentration generated (shaded column on the table) was considerably higher when the 'fixed' power supply was used (650 vs. 230 ppb), despite the fact that there was less ionisation time. It is noteworthy that the Arduino overall displayed a higher average current (stabilisation was not achieved due to the short switching time of 15 seconds, as described above), interpreted as follows:

Max. current = 3.16 mA
Min. (after 15 sec) = 1.71 mA
Average = 2.43 mA
Which compares to the 2.08 mA generated by the fixed power supply.

The assumption above can be safely made given that the decrease in current from peak to stable values was observed to proceed at a roughly linear (constant) rate, though this wasn't precisely measured. A more sophisticated instrument such as an oscilloscope would have been required for this purpose, but it suffices to observe that currents were overall higher (both peak and stable) in the Arduino, while generating considerably less silver ions.

The total stabilisation time needed is seen to be 1 – 2 min for most cases, implying that the switching period set in the original power supply used in the field (10 sec) is too small and does not allow enough time for the current to settle. Much of the energy consumed is used to overcome the polarisation of the water, rather than releasing ions which is the final objective of the device. Given the large peaks (Ipeak) observed compared to the stable current values, this energy inefficiency can be quite significant, as shown in the following section, and needs to be considered in improved system designs.

5.4.5.3 Power consumption

The general formula for power consumption of any electric device is as follows:

$P\ (Watts) = V \times I$ [5.3]

Where Voltage is in Volts and Current (I) in Amps. Using the data from Table 5.33, we can see that the average current value for the full-cell device in RW is 4.2 mA, for a voltage of 4.85 V and an average conductivity of 82.8 μS/cm. Using the above equation, power consumption would be equal to:

$P_{ave} = (4.85\ V)\ (4.2\ mA) = 20.4\ mW$

In the case of tap water (using the lowest voltage value in Table 5.31), this would increase substantially to:

$P = (25\ mA)\ (5.1\ V) = 127\ mW$

Evidently with higher voltage settings this amount is bound to increase, but for the sake of comparison, only values in the range of 5 V, which is the most common setting in the field, will be examined. The effect of switching and peak surges discussed in the previous section, becomes an important factor when considering power and energy consumption. Using the values on Table 5.39, at a similar conductivity and voltage setting as the example above for RW (though using silver rods), the following comparisons can be drawn:

Switching device (Arduino):
$P_{peak} = (4.91)\ (3.16) = 15.5\ mW$
$P_{low} = (4.91)\ (1.71) = 8.4\ mW$ [28]

Average power consumption, assuming a roughly linear current drop for each cycle, would be: $P_{ave} = 12.0\ mW$

Fixed power supply:
$P_{constant} = (4.96)\ (2.08) = 10.3\ mW$ (discarding power loss for peak values, since these would only occur at the start of the ionisation process).

[28] This refers to the lowest current value reached at approx. 15 sec, before switching polarities.

Table 5.40. Silver yield related to power consumption

Power supply	Power consumption (mW)	Ag concentration (ppb)[1]	Total silver mass (mg)[2]
Fixed	10.3	650	0.52
Switching	12.0	230	0.18

1. Data obtained from Table 5.39

2. Total silver generated in experiment = concentration (µg/l) x 0.8 L (since volume ≈ 800 ml)

Table 5.40 summarises these values, showing that despite the switching device consuming more average power, the resultant silver mass released into the water by the silver rods is considerably lower, at roughly the same conductivities and ionisation times (4 min). Since the target of the system is to release silver ions, this implies that the same goal can be achieved by lowering the voltage (consuming less power) and extending the switching period (possibly in the range of hours or minutes, rather than seconds), minimising the effect of current reversal peaks, while still protecting the electrodes from scaling.

These current peaks were observed on different devices and water sources. The SilverLife power supply, used in the field, operates essentially the same as the Arduino supply used for the experiments above, except with a lower period (10 sec), which implies even less power inefficiency in the generation of metal ions.

5.5 SUMMARY AND DISCUSSION

5.5.1 CONDUCTIVITY

Conductivities are expected to vary overall as the concentration of silver ions in the water increases. This can be shown by the unequivocal increase with electric current (Section 5.4.2) that occurs upon ionisation. Given that current (I) is related strictly to voltage and resistance (Ohm's Law), and voltages remain constant throughout individual experiments, any rise in current can be explained as a corresponding rise in conductivity (which is inversely related to resistance). However, as discussed in Section 5.1.1.1, conductivity variations for the relatively low silver ion inputs used here (in the order of ppb) are usually too small to be detected by the conductivity meters available in the lab. Changes in readings are more likely attributed to measurement error than to an actual increase, except in the case of DI, where there are less interfering ions to start with and readings tend to be more stable.

Table 5.41 compares a selection of data for different water types and silver concentrations. The particular device used to achieve this concentration is not relevant in this case, but rather a simple comparison between the initial and final conductivity measurements. A paired samples t-test for all 27 samples shows there to be no significant difference in the means ($p>0.05$ for each water type). Only in DI is an upward trend observed, but is still not statistically significant within a 95% CI, given the low number of samples ($p = 0.095$).

In order to test for this general positive correlation between conductivity and silver ionisation, an extreme case experiment was performed. Conductivities were measured in DI water before and after the addition of a Jenway 1,000 ppm Silver Standard solution, in a 1:100 dilution, (1 ml of standard in 99 ml of DI) for a total expected concentration of 10 mg/l (10,000 ppb). Conductivity rose from 1.6 to 190 µS/cm upon addition of the standard, proving the significant increase that can occur when silver is present in high enough concentrations.

Table 5.41. Comparison of conductivity variations

Water source	Sample No.	Silver (ppb)	Ionisation time (min)	Conductivity initial (µS/cm)	Conductivity final (µS/cm)
DI	1	410.0	10.2	2.0	4.0
	2	<10	10.0	2.0	2.5
	3	706.0	230.0	1.5	3.0
	Mean			1.83	3.17
RW	1	460.0	11.0	52.5	52.0
	2	670.0	17.5	170	161
	3	830.0	10.2	120	122
	4	730.0	71.0	94.0	93.4
	5	650.0	4.0	79.5	80.3
	6	60.0	1.0	82.4	80.4
	7	90.0	1.0	73.9	69.2
	8	60.0	4.0	73.9	68.4
	9	70.0	8.0	73.9	68.5
	10	10.0	4.0	66.6	65.4
	11	160.0	1.0	70.0	72.2
	12	190.0	4.0	70.0	73.2
	13	190.0	8.0	70.0	72.0
	14	70.0	8.0	70.0	66.9
	15	60.0	8.0	76.2	69.3
	16	60.0	4.0	68.6	64.9
	17	770.0	5.0	117	116
	18	710.0	8.8	117	112
	19	690.0	8.8	117	120
	Mean			87.5	85.6
TAP	1	910.0	22.0	531	493
	2	940.0	7.0	670	693
	3	705.0	10.0	770	790
	4	50.0	3.0	692	661
	5	850.0	5.1	692	673
	Mean	27	27	671	662

5.5.2 pH AND ALKALINITY

Though pH was measured and monitored in many of the samples (Section 3.3.2), it is not a variable that was specifically controlled, as this would have implied the addition of chemicals to test waters (i.e. sodium bicarbonate to increase pH), which in turn could have produced unwanted effects such as increased complexation and eventual precipitation of silver ions (Landau 2007). In theory, pH should increase with ionisation, according to the reactions shown below (Kegley & Andrews 1998; Delahay et al. 1951).

Auto-ionisation of water: $H_2O = OH^- + H^+$ [5.3]

Anode (positive cell): $Ag \rightarrow Ag^+ + e^-$ (release of silver ion and one electron)

Cathode (negative cell): $2H^+ + 2e^- = H_2$ (evolved as hydrogen gas)

The removal of these hydrogen ions (or protons) from the water will form an alkaline layer close to the electrode, with a corresponding increase in pH. Depending on the water hardness, calcium or magnesium carbonates may then form and adhere to the surface of the cathode. This phenomenon, known as 'passivation' and equally applicable for other metals such as copper, can greatly obstruct the ionisation capacity, causing the system to demand more energy and operate inefficiently, with the risk of burning or damaging one of the electrodes, in extreme cases. Besides the formation of scale on electrodes, excessive hardness can also create problems by precipitating silver ions, making them unavailable for disinfection. In practice, if water is naturally soft (as is common in RWH) or artificially softened, UK guidelines suggest that residual silver concentrations can be reduced with the same disinfection effectiveness, from 40 to 20 µS/cm (Health and Safety Executive 2000, p.50).

This is the main reason behind the 'switching' of polarities used by many commercial devices, including the ones used in the field for the present project as discussed in 5.4.5.2. By alternating the roles of cathode and anode the reactions above are reversed, removing any scale that may have become attached to the electrodes. If a fixed polarity is used, then the reaction taking place at the cathode can be predicted by a Pourbaix diagram (Delahay et al. 1951) which postulates that the higher the pH, the more likely that passivation will occur for a given electric potential (voltage). Conversely, lower pH values will have a greater threshold where corrosion (i.e. release of metal ions) can occur with higher potentials (Figure 5.14). The implications of this have been confirmed in practice. In a study on a silver ion system used for Legionella control, high pH values were found to adversely affect disinfection efficacy (Lin et al. 2002).

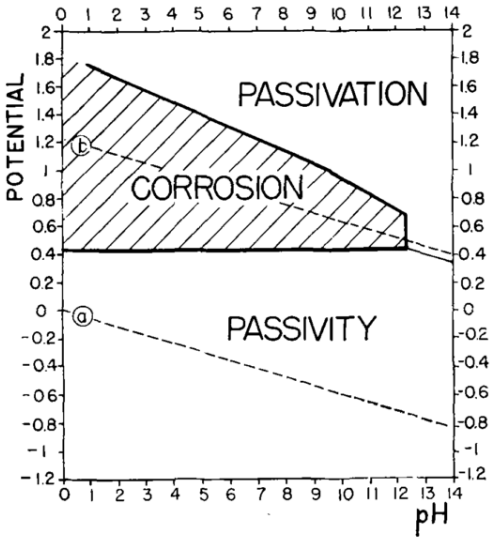

Figure 5.14: Pourbaix diagram for silver at 25ºC (Delahay et al. 1951)

In the case of RWH, the topic that concerns this work, pH tends to be slightly acidic, as well as containing relatively low hardness and alkalinity (Adler et al. 2011; Lee et al. 2010; Meera & Ahammed 2006), which will favour the operation of the ionisation device used. Cation analyses in the lab (Table 3.9) and in field samples (Table 4.3) revealed consistently low calcium and magnesium concentrations, the main sources of water hardness. The inverting of polarities should also be enough to prevent excessive formation of scale, though it can still occur and needs to be incorporated into a maintenance routine. If longer switching periods are used to improve power efficiency, as suggested in 5.4.5.3, then an interesting option to reduce scale formation would be to explore the use of lower voltages, below the thresholds defined by Pourbaix diagrams for passivation[29]. However, with the ensuing drop in electric current, ionisation would proceed at a slower pace and care must be taken to ensure that sufficient silver ions are available in the water for disinfection.

As with conductivity (section 5.5.1), pH variability during ionisation was difficult to measure, due to instrument imprecision or to the small changes that would potentially occur in these experiments, where silver ion addition was relatively low. Where pH was measured, it is shown in the data set on Annex A. In general terms, tap water had the highest pH, with RW and DI tending to be more acidic. In some experiments pH was shown to increase slightly after ionisation, and in others to decrease or remain

[29] This is roughly 1.6 V for pH = 7 and Temperature = 25ºC

stable. Furthermore, on occasion a pH reading would be higher, but on a second reading (of the same sample) be lower than the starting value (previous to ionisation). Thus, no relevant conclusion can be drawn here.

5.5.3 CHLORIDE

One of the most common precipitates that form in the presence of silver ions in natural waters is silver chloride. Rainwater was seen to have relatively low initial chloride concentrations which were not seen to change significantly upon addition of silver in any of the experiments performed in the lab (see 5.1.6.1 and Table 3.8). This could also be due to instrument variability (Ion Chromatograph) within the low ranges measured.

An additional test was performed using a Chloride Meter (3.3.5.1), by adding 5 ml of a 600 ppb solution (electrolytically generated using the half-cell device) to 95 ml of pure RW from the external butt. Thus, a 1:20 dilution was done on the original silver solution. In theory, assuming no precipitation or complexing, this would produce a 30 ppb concentration (10 ppb was actually measured). The conductivity of the RW used was 50 µS/cm. A control and the prepared sample were read for chlorides after 15 min, obtaining the following values:

Table 5.42. Chloride variations in RW with silver ion addition (values in mg/l)

	Description	Cl^- (1^{st} reading)	Cl^- (duplicate)
Sample	95 ml RW + 5 ml 600 ppb Ag	9	6
Control	(100 ml pure RW)	5	2

Duplicates were taken, as the readings were found to be variable and a slightly unstable. Nevertheless, Table 5.42 shows a substantial chloride reduction, although statistical significance cannot be determined given the small sample size. The lowering of silver concentrations in RW as compared to DI shown in Section 5.1.6 is also a clear indication of precipitation and/or complexing of the silver ions due to interacting anions in RW.

Silver chloride has a low solubility product (Benjamin 2002, p.45), meaning that once formed it will not dissociate easily into silver and chloride. Some authors, however, suggest that it is a photosensitive compound, that in the presence of light silver chloride will decompose into metallic silver and chlorine gas (Landau 2007, p. 20), though this was not experimentally confirmed here. Chlorine has been proven to have a synergistic effect with silver ions for the elimination of various microorganisms (Landeen et al. 1989; Yahya et al. 1990), so this photosensitive release could have positive implications. The mechanism of metal-ligand formation and solubility is highly complex and is temperature dependent, among other factors. A further discussion of this, beyond the scope of the present work, can be found in Choppin (2004).

5.5.4 TURBIDITY

From the experiments with Model II (Section 5.2.2), a clear positive correlation can be observed between increases in electrolytically generated silver concentration (i.e. using the ionisation devices) and turbidity. This phenomenon can be attributed to the formation of the precipitates upon reaction between the silver ions released from the anode and free ions in the water. These precipitates are likely to contain silver chloride (AgCl), calcium and silver oxides, according to Landau (2007) and Delahay et al. (1951). During ionisation, as noted in the visual observations of various experiments, a white 'cloud' can be physically seen in the water, with greater intensity in tap water than in RW (possibly due to higher conductivity and/or ionic strength[30]).

It is worthy of note that this phenomenon was not observed when using concentrated silver standards (i.e. turbidity remained unchanged after silver addition). This could be due to the very high dilution of the original standard to achieve similar concentrations to those reached by electrolysis. The laboratory standards used all contain a silver concentration of 1,000 ppm. This means that a 1:1000 dilution would potentially produce 1,000 ppb Ag in water. The data plotted below consists of electrolytic silver concentrations which are lower than this.

Figure 5.15 shows the relationship between turbidity and silver concentrations for tap water, RW and DI. The data was obtained using Model II and selected batch experiments where turbidity was monitored. A significant correlation can be observed in both tap water and RW with a 95% CI, but not with deionised water (DI), where the near absence of potentially precipitating ions and the low current generated (due to low conductivity) account for the lack of change in turbidity. At the opposite end of the spectrum, tap water shows the highest variation. Correlation coefficients and relevant data are summarised in Table 5.43.

[30] Ionic strength is defined as the composite effect of all ions in a solution, closely related to conductivity/ TDS (Benjamin 2002)

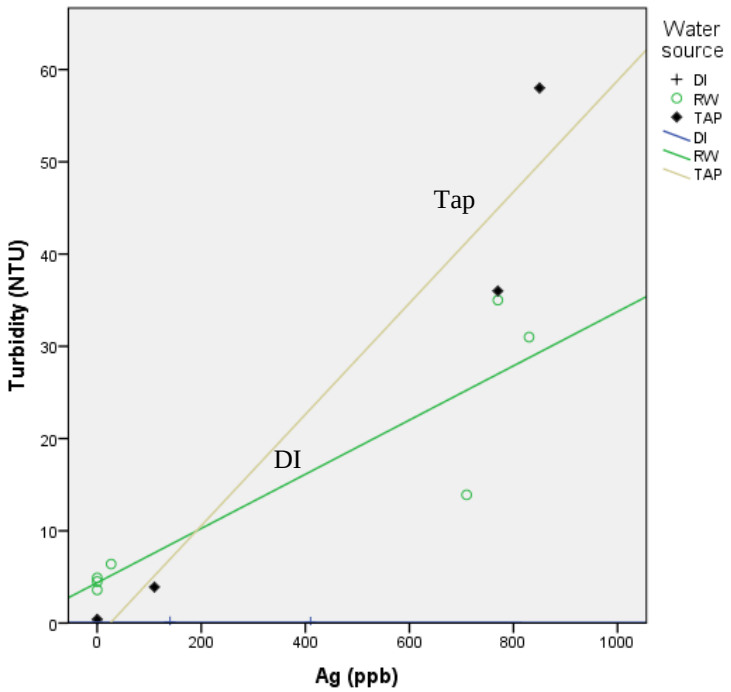

Figure 5.15. Silver and turbidity correlation (SPSS output)

Where flow is concerned, evidently turbidity will be affected as the silver-containing particles are carried away. In continuous flow tests using Model I, turbidity was seen to remain relatively constant for different silver concentrations (Mean=1.26, SD=.21), with flow ≈ 1 Lpm throughout. These samples were thus excluded from Figure 5.15 and the ensuing statistical analysis shown here.

Table 5.43. Correlation coefficients from turbidity experiments

Water source	Coefficient (r)[1]	Significance (p)	[2] Equation
Tap	0.90	.003	1.51 + 0.06 x
RW	0.97	.017	4.38 + 0.03x
DI	0.18	.44	Not correlated

1. Pearson's correlation coefficient
2. Equation of regression line (b+mx), where x represents Ag concentration (ppb)

5.5.5 DISINFECTION

There is ample reference in the literature as to the disinfection capacity of silver, the minimum inhibitory dosage required for a variety of microorganisms and the cellular mechanisms involved, which are discussed in 2.3.3.5. The experiments described above show a complete removal of the indicator microorganism (*E. coli*), with silver concentrations as low as 50 ppb (Sections 5.1.1.3, 5.1.4.1 and 5.3.3). In batch experiments, reaction time was at the most 20 min, showing that residual silver in the tanks will react rapidly with remaining microorganisms, ensuring adequate drinking water quality as long as the silver is periodically dosed (Nawaz et al. 2012).

In continuous flow, the full-cell device achieved concentrations much higher than 50 ppb, usually in the range of 100 – 200 ppb, with flow rates commonly utilised in the field (approx. 1 Lpm). Model I (using pump and filtering) was not adequate for testing bacterial disinfection, as explained in the methodology, but in Model III (gravity flow), inoculation was successfully performed. In this case, using slightly slower flow rates than with the pumping system of Model I, complete removal of the indicator organism was achieved in continuous dosage, with reaction time < 1 min and a silver concentration of over 200 ppb (Section 5.2.3.2).

An experiment using silver standards (Section 5.1.4.1) shows that the availability of silver ions is greatly diminished after disinfection when high initial amounts of microorganisms are present, probably due to retention in the bacterial cell walls or DNA interaction (Gerba & Thurman 1989). In the case of bacteriophages, which as viral particles are more resistant to disinfection in general (Grabow 2001), the limited testing described in section 5.3.2 shows concentrations of 200 ppb Ag to be enough for the inhibition of moderate counts of somatic coliphages in RW (2-log removal approx.). This concentration is shown to be achievable by the full-cell device in lower flow rates, as described above. However, coliphages were not observed in any raw rainwater samples (in the lab), though analyses in the field could not be performed. More data would thus be needed in order to safely draw conclusions as the efficacy of the device for viral removal.

5.5.6 SILVER

5.5.6.1 General model using Faraday's law

The release of silver ions into water by electrolysis is governed mainly by Faraday's law, which states that the amount of metal released into the water is directly proportional to the electric current passing through the electrodes. For the simplified case of constant, direct current, this can be stated mathematically as follows (Roberge 2012; Landau 2007):

$$\boldsymbol{m = \frac{ITM}{Fz}} \qquad [5.4]$$

Where,
m: mass (g) of metal liberated into the water
I: DC current (A) flowing through electrode
T: ionisation time in seconds
F: Faraday's constant (≈ 9.6485 x 10^4 Coulomb/mol)
M: Molar mass, or atomic weight, which in the case of silver is 107.9 g
z: Valence or charge of the metal ions (z = 1 for Ag+)

The last three terms are constants, implying that, in principle, only ionisation time and current will determine the amount of silver ions being released into the water. In practice, however, electric current in a liquid is a complex variable dependent on several factors. According to Ohm's law (equation 5.2), current is strictly related to the voltage and to the resistance of the conducting media. Simple though this may

seem, the computation of electric resistance in water poses numerous challenges. In a solid conductor, the calculation is straightforward:

$$R = \rho \frac{L}{A} \qquad [5.5]$$

Where ρ is the *resistivity* of the substance measured in Ohm.m (Ω.m); L is the length of the conductor and A the cross-sectional area. If the analogy were drawn to water, then the distance and volume of liquid between the two silver electrodes would be determinants to the total resistance, as well as the *conductivity* (which is the reciprocal of resistivity)[31]. However, the free ions that conduct electricity in a liquid don't behave in the same orderly manner as electrons in a solid copper conductor. The movement and dispersion of such ions is extremely complex and hard to predict. Inserting the probes of a resistance meter (or multimeter), which was attempted in the lab, will give highly variable readings, according to the erratic movement of such ions, besides being dependent on the depth and distance of the meter tips.

Some authors suggest using the surface area of the electrodes as the cross-sectional area of equation 5.6 (Roberge 2008), assuming the ions will travel in the shortest possible distance along the electric field. In waters with relatively low interference (i.e. low TDS or conductivity), this could be a good approximation. With this assumption in mind and substituting into Ohm's law (5.2):

$$I = \frac{V}{R} = V \frac{\sigma A}{d}$$

Using the following units for consistency with the measured data:
Current (I): µA
Conductivity (σ): µS/cm
Area (A): cm^2
Distance between electrodes (d): cm

Substituting this into equation 5.5, and considering that silver concentration (ppb or µg/l) is equivalent to the silver mass (µg) released at the electrode divided by the total volume (l), the following is derived:

$$Ag\ (ppb) = Co \frac{V\sigma AT}{(d)(Vol)} \qquad [5.6]$$

[31] The SI unit for conductivity is Siemens/metre (S/m)

Where Co is a constant which, according to equation 5.5, is equivalent to:

$$Co = \frac{M}{Fz} = \frac{107.9g}{9.65x10^4} = 1.12x10^{-3}\ g/Coulomb$$

Since z = 1 for monovalent silver. Coulomb is a measure of total charge, related to current as 1 Amp = 1 Coulomb/second. The units in equation 5.7 thus are consistent as long as time (T) is in seconds and Volume (Vol) is in litres. Conductivity (σ), as expressed above, would need to be in µS/cm in order for the desired result to be in µg/l (or ppb).

Equation 5.7, in essence, provides a theoretical framework for obtaining a target silver concentration in batch procedures (fixed volume), using parameters readily measured and obtained in the lab. Complications would arise upon the introduction of flow in continuous operation, where the silver ion concentration would be diluted. Particularly where filters are involved (5.2.1.1), the mathematical prediction becomes increasingly complex. In fact, flow (Q) and silver concentrations were found to be uncorrelated in the data set collected for Model I ($p > 0.1$). Furthermore, if silver saturation values (whether in solution or in the filters) are also taken into account, the equation becomes non-linear. More data than that obtained here would have been needed to adequately model such a relationship.

Another assumption from equation 5.7 is that 'fixed' power supplies are used. Switching polarity supplies, such as the ones used in the field (see 3.3.1.3), were observed in the lab to have implications on electric current and silver ion generation (5.4.5), which are not reflected in the equation.

5.5.6.2 Linear regression

Using the experimental data obtained for batch experiments (no flow conditions) where only a fixed power supply was applied, the equation described above can be statistically tested and any divergences examined for practical implications. The data set itself can be consulted in Annex A. In the case of the half-cell device (Figure 3.7), for which most batch experiments were performed and thus more data is available, equation 5.7 becomes:

$$Ag\ (ppb) = Co\left(\frac{A}{d}\right)\left(\frac{V\sigma T}{Vol}\right) = 1.12x10^{-3}\left(\frac{3.1}{2}\right)\left(\frac{V\sigma T}{Vol}\right) = 1.73x10^{-3}\left(\frac{V\sigma T}{Vol}\right)$$

[5.8]

The surface area of the electrodes as well as the distance is taken from Table 3.5, expressed in cm^2 and cm respectively, in accordance with all other units used. Equation 5.8 then becomes a theoretical model for the half-cell device, given the constraints described above. The variables shown on the right hand side in parenthesis (Voltage, conductivity, etc.) are all relatively straightforward to measure.

Obtaining the value for current in an experiment greatly simplifies the calculation (Equation 5.5), given that current already 'groups' together several factors, such as voltage, surface area and conductivity, and provides a more precise result, with less variables to be measured. However, it is not always easy to measure current directly,

as the circuit must be 'intercepted' by the meter, which poses several logistical constraints in practical applications (3.3.1.3). Voltage is not only simpler and safer to measure; it is also the main control variable on the devices installed in the field, and the only one to which the end user actually has access.

A linear regression model for the half-cell device would then take the following form:

$$Ag\ (predicted) = Bo\left(\frac{V\sigma T}{Vol}\right) \qquad [5.9]$$

Where Bo would be the regression coefficient. Theoretically, this is predicted from equation 5.8 to be $1.73x10^{-3}$, since Area (A) and distance (d) are constant for this particular device. The test would thus consist in comparing the experimental coefficient with the theoretical.

The linear regression performed in SPSS with the data (N = 23) is shown in Table 5.44 and Table 5.45. Evidently, the model will be start at the origin (constant coefficient= 0) since when voltage or time are equal to zero, current (and thus silver ion release) will also be zero. Residual silver in the ionising vessel or trace quantities in test waters are not taken into account. Two outliers were removed (Cook's distance > 1), incidentally corresponding to points where silver saturation values had probably been reached in solution and were thus outside the linear range (see discussion in 5.1.1.1), reducing the sample size to N = 21.

Table 5.44. ANOVA table for linear regression using the half-cell device

	Sum of Squares	df	Mean Square	F	Sig.
Regression	1676278.427	1	1676278.427	29.173	<.005
Residual	1149196.351	20	57459.818		
Total	2825474.778e	21			

Note: Ag (ppb) is the dependent variable

Table 5.45. Summary of linear regression model

Model parameters	Coefficients
R = .770 R^2 = .593 Adj. R^2 = 0.573 SE of estimate = 239.7	Bo = $0.3x10^{-3}$ (SE = $.064x10^{-3}$) β = 0.770 t = 5.401 p < .005 (.000028)

β: standardised coefficient; SE: Standard Error; Bo: unstandardized coeff.

The model can be seen to be strongly linear (r = .77) with a high level of significance (p<.005), which confirms the theoretical basis for linearity described above. The predicted Bo coefficient ($0.3x10^{-3}$), also highly significant, is relatively close to the theoretical value ($1.73x10^{-3}$). The differences between them can be considered to be small, given their order of magnitude, particularly when compared to the other

parameters in equation 5.8. Area and distance are expressed in cm, about 1000 times larger than Bo. Thus, small errors in the measurement of surface area (i.e. ± 0.1 cm), for instance, will have a high impact on the calculated linearity coefficient, if inspected at the 10^{-3} order of magnitude.

Other differences could be attributed to the fact that resistance is not exactly proportional to the surface area of the electrode, but might depend on other unpredictable factors, such as the movement and interaction of other ions in solution, or the presence of microorganisms, which might attach free silver ions to their cells, reducing their availability as transporters of electric charge (Gerba & Thurman 1989). The interaction of charged ions with the borosilicate or polycarbonate walls of a glass container, for example, could also be factors affecting the amount of current flowing between the electrodes, particularly if the vessel is small compared to the total volume of solution (Struempler 1973). Despite these potential sources of errors and the relatively low sample size, the linear model is seen to be a reasonable fit of the data, confirming that equation 5.9 could be used in practical situations, as long as the variables are precisely measured and the experimental constraints described are taken into account.

5.5.6.3 Cell position and retention time

An additional effect linked to the ion concentration generated is linked to the design of the actual ionisation device, particularly when dealing with continuous flow situations, which are most common in practice. As discussed in the methodology (3.3.1.1), one of the key differences between the lab system (full-cell device) and those installed in the field is the size of the ionisation chamber. In the field this is no more than a PVC 'T' connector, with little or no retention time, while in the lab this consists of a vessel of approximately 300 ml. This provides for an additional retention time, which will undoubtedly affect the accumulated concentration of silver ions during the ionisation process.

The position of the cells (i.e. coins), then, becomes important. If these are located parallel to the flow, the liquid will flow from one end of the vessel to the other as quickly as possible, reducing the possibility of exposure to the silver being generated by the cells. When these are perpendicular to the flow, however, the incoming water will be forced inside and around the vessel, indirectly increasing retention time. Many of the more complex commercial systems available take advantage of this fact, by designing systems where the water is channelled throughout various parts of the system for as long as possible (Tarn-Pure 2013; AquaLyse 2013), much in the manner of commercial chlorination systems.

The experiment shown in Section 5.2.3.1 for Model III (gravity flow), shows a marked increase in silver ion generation when changing the cell orientation from parallel to perpendicular (from 670 ppb to 920 ppb) for similar flow rates and experimental conditions (same water source). This represents a silver concentration increase of nearly 40% (samples were taken after 1 min in both cases). From Table 5.24 in this section it can be observed that electric current does not vary substantially

from one case to the other (around 6 mA in both cases). In all likelihood, the silver ion increase is thus attributable to a corresponding variation in retention time, caused by the change in cell positioning.

When increasing the sampling time and the flow rate, however, the effect of cell position seems to become less marked. The last two runs shown in Table 5.21, for instance (numbered 4b and 6), correspond to similar experimental conditions except that in the first one (4b) the cells are in parallel, while in the second one (6) cells are perpendicular. The difference in silver concentration is only 10 ppb (from 190 to 200 ppb), which could be attributable to other external factors, or to the fact that ions are being carried away at a rate fast enough to make the effect of a longer retention time in the vessel less significant. A more detailed investigation of this effect would require an extensive fluid dynamics analysis of water flow throughout the device, which is mentioned here as a recommendation for future work.

The following chapter contains a general discussion based on all the results described above as well as the fieldwork data from Ch. 4.

6 GENERAL DISCUSSION

This chapter presents an overall discussion of the research project as a whole, starting from an evaluation of the fieldwork results, comparing the progression between both sampling periods, as well as an assessment of variation in the parameters of individual sites. This is followed by a section discussing the possible impacts and lessons learned from the laboratory work that could be applied in the field, a matter that is further elaborated in the conclusions (7.2). The last two sections of the chapter cover possible sources of error in the field and in silver measurement (6.3), which is a critical factor, followed by an extensive yet highly appropriate analysis on socially sensitive issues, such as maintenance and adoption of the technology (6.4).

6.1 APPRAISAL OF FIELDWORK RESULTS FROM 2010 TO 2012

Table 6.1 shows a comparison between the 2010 and the 2012 samples at the drinking tap, after filtration and disinfection with silver ions (the data is taken from Tables 4.1 and 4.5). Cistern measurements, as well as settling tanks, tend to vary seasonally and according to the maintenance provided in each case (see Section 4 below), but parameters at the drinking tap should, ideally, comply with high quality standards regardless of internal variations throughout the system.

Table 6.1. Comparison of field parameters at drinking tap

Parameter	**2010**	**2012**
Temp. (°C)	22.8 (2.0)	19.4 (1.1)
pH	6.8 (0.1)	6.8 (0.1)
Conductivity (µS/cm)	110 (17.3)	145 (48.6)
COD (mg/l)	6.4 (2.4)	2.3 (1.1)
DO (mg/l)	2.8 (0.4)	4.8 (0.3)
Hardness (mg/l)	67.8 (19.0)	42.3 (5.9)
Alkalinity (mg/l)	73.3 (23.1)	27.8 (4.6)
TOC	NA	1.8 (0.6)

Note: mean values shown with SEM in parenthesis

Despite the fact that the second sampling round was more thorough, with more samples taken along with additional parameters (such as TOC and silver), an overall comparison can still be drawn by inspecting Table 6.1. Conductivity is seen to be higher on the average in 2012, which could be related to the higher number of samples, or more particle accumulation in the filters. However, values are still within what can be reasonably expected for rainwater (Kegley & Andrews 1998). COD seems consistently lower in 2012 (with correspondingly low TOC values), which

indicates increased effectiveness in reducing organic loads. On a related note, the removal of microorganisms also seems to improve in the second round compared to the first. Table 4.2 shows that a small number of total coliforms were found in some of the drinking taps in 2010 (though not high enough to be of concern; all values are under 5 CFU/ml), while in 2012 a complete removal of all bacteriological indicators was achieved, even when more samples and duplicates were taken (Table 4.6).

One particular system (discussed in section 6.4.2), which had important failures and cross-contamination of the cistern in 2010, showed effective disinfection and better overall performance in 2012. Such improvements in the second round are hard to attribute to any specific factor, and are more likely a combination of several variables, not least of which is maintenance and community participation. It must be noted that the silver cells had not been replaced in any of the systems for more than 2 years (since installation). In most of the sites there was still silver left (Figure 6.3), but in one of them (Site No. 6, Table 3.1), they were almost entirely depleted (Figure 6.1). Such differences in silver cell content are not related to bacterial load or contamination, but solely with the amount of current flowing through the device. As explained in 5.5.6.1, this is linked mainly to voltage and water conductivity. The latter varied from site to site, but not enough to account for such a high difference in cell consumption. Voltage was fixed at 5V, and had apparently not been purposefully modified in any of the systems. Thus, the different cell degradation patterns in are more likely due to the following causes:

- Power failures: some of the communities had frequent power interruptions, which could account for silver being consumed at a slower rate. Site No. 1 (referred to in Figure 6.3), for instance, had a highly inconsistent and unreliable electric supply – notwithstanding, it was one of the better performing systems, possibly due to a more engaged community with more maintenance activity (see Section 6.4.4).

- Short circuits: In some cases, the accumulation of scale and debris over time can damage the electrodes (5.5.2). As the power supply attempts to feed current through a reduced area, this will inevitably increase the current density, much in the same manner as compressing a fluid through a clogged pipe. The coating formed around the electrodes can also reach the extreme of ‘bridging the gap’ between them, creating a short circuit. Although the devices are usually fitted with protective fuses, the higher currents can easily consume the electrodes at a rapid pace before these are triggered (Figure 6.2).

Silver was found to some extent in all of these systems in 2012 (Table 4.5), indicating that any damage or excessive silver consumption of the cells had only happened recently. The fact that, even on the site shown in Figure 6.3, a complete removal of microorganisms was attained, could be pointed out as a proof of the robustness of the silver ion system, as it is unlikely that the disinfection levels obtained could have been achieved by using filtration alone. The pore sizes of conventional sediment cartridges and carbon filters allow most micro-organisms to pass through (WHO 2008). In fact, colonization of bacteria and recontamination is a common occurrence, given the large surface area and adsorption capacity of granular activated carbon (Bitton 1994). All

the systems evaluated for this study had already been in use for at least a year, at the time of the first sampling round, without any replacement of carbon cartridges, thus allowing biofilms to accumulate.

Figure 6.1: Consumed silver cells in San Miguel Viejo (2012)

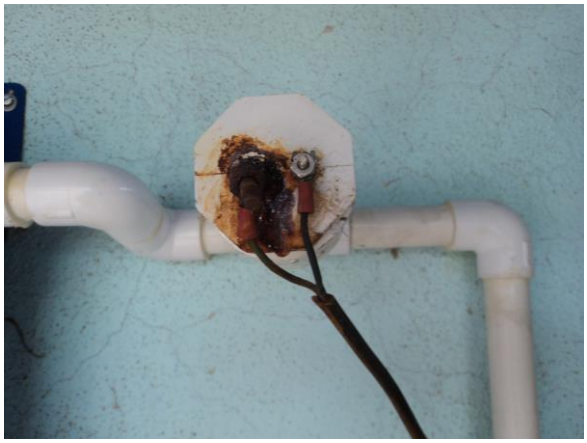

Figure 6.2. Effects of over-current in San Miguel Viejo

Figure 6.3. Silver cells (after cleaning) in Rancho Nuevo (2012)

6.2 APPLICABILITY OF LAB TESTS TO THE FIELD

Among the main lessons learned from the lab work that could be potentially applied to the field, whether on future or existing systems, are the following:

a) Redesign of the silver ioniser: It was observed that adding a vessel for holding the silver cells, as well as rotating these to be perpendicular to the flow (instead of parallel) will increase the retention time, and in consequence the silver concentrations reached at the ioniser output. This would ensure a more effective disinfection than the same amount of silver dispersed throughout the pipes at lower concentrations, which could breed resistant strains (Silver 2003) or be insufficient to guarantee inhibition of all pathogenic microorganisms. Bacteriophage tests (0) have shown that more silver is needed where viral particles are suspected than what is commonly used for *E. coli* and traditional bacterial indicators (Jung et al. 2008; Yahya et al. 1992).

b) Extend the switching period of the power supply: The experimental results have shown that the current polarity inversion time of 10 – 15 sec used in the field is insufficient to allow an optimal use of the device, reducing current flows and silver ions generated, as well as using electricity inefficiently due to current 'peaks' associated with the capacitance effect of water (5.4.5). If two identical electrodes are to be used, as it is presently done[32], then a switching period of 60 min, for instance, would protect excessive scale from forming around a single electrode, while using power more efficiently and increasing the silver ion production. Further testing would be required to precisely determine this optimal period.

c) Variations in turbidity could act as a fast and cost-effective indicator of silver ion generation at a specific point, provided that samples are analysed soon enough and that initial turbidity is low, as well as relatively constant (i.e. RW has been pre-filtered up to a minimum standard before application of the silver ioniser). This procedure would require the previous calibration of a 'turbidity-silver curve', as well as abundant confirmative testing in the field to determine the level of accuracy attainable (see suggestions for future research in section 7.2).

d) Positioning of device: At present, the ionisation device is placed after the prefilter and before the 2-stage filters. Depending on the final objective this position could be changed. Experimental runs show a considerable silver reduction in the 2-stage filters, possibly due to the GAC/KDF component (5.2.1), indicating that of all the lab setups

[32] There are other systems that do not switch polarities but rather use a 'sacrificial' electrode of another material (i.e. steel); or contain separate copper and silver electrodes (Stenulson 1998; Landau 2007)

for continuous flow described in section 3.3.3, Model I yields the most optimal results which are applicable to the field, ensuring compliance with existing WHO guidelines for maximum silver concentrations (WHO 2008). Even though silver ions in the relatively low concentrations applied here have not been shown to be harmful to humans, it might still be desired as a cautionary principle to reduce the intake, while guaranteeing disinfection. The disadvantage is that in systems which are not used for a prolonged period (such as schools during the summer holidays), may not have enough residual silver in the final pipeline and drinking tap to protect from contamination or biofilm formation. This might be partially addressed, however, by letting the systems flush for a while before resuming operation, to increase the flow of ions through the output and rinse the pipes. Emptying pipes of any residual water before such a suspension period could also be an option, albeit more difficult to ensure that it is adequately done in the communities.

6.3 ERROR ANALYSIS

Some of the possible sources of error are listed below:

a) Silver measurement (see 6.3.1)

b) Fieldwork limitations (see 6.3.2)

c) Conductivity and pH measurements
(use of different instruments with varying precision)

d) Instrument calibration inadequate for the low concentrations found in RW
(IC, TOC, ICP-OES, etc.)

e) Accuracy in physical measurements of ionisation devices
(surface area, weight, volume)

f) Non-uniform source water characteristics (i.e. pH variations in DI and tap water)

The list is not extensive. However, the first two items deserve special attention, as they are considered to be most relevant to the present research.

6.3.1 NOTES ON METHODOLOGY FOR SILVER MEASUREMENT

The measurement of silver was considered crucial to this project. Thus, a considerable amount of time was invested in finding and testing the right method. These are listed in 3.3.5.1. Ideally, the same instrument should be used throughout an entire research project in order to allow for better comparisons. However, Hach spectrophotometry, used in the lab due to its convenience and the possibility of on-site testing, was not available in the field, where storage of samples for analysis with ICP-MS was found to more convenient. The two methods were compared with known samples in DI water, showing a significant divergence for values higher than 30 ppb (Table 6.2). Several issues are at stake here:

- The ICP-MS has a calibration range of 0 – 30 ppb. Any samples with higher expected values need to be diluted, creating an additional source or error. Furthermore, the instrument methodology suggests that samples be filtered (APHA 2012). The first two lines in Table 6.2 show a reduction in measured silver in the filtered samples compared to the unfiltered ones. This has implications for comparison with lab work results, as Hach samples were not filtered (since it is not required for the colorimetric detection method used).

- The Hach instrument reads in the mg/l or ppm scale, with a level of accuracy of ±5 ppb and a lower detection limit of 0.1 mg/l (10 ppb), making it unsuitable for very low concentrations.

- The ICP-MS was not always available, but had to be booked, sometimes months in advance. This created a potential source of error related to prolonged sample storage (both in fieldwork samples which had to be delivered from Mexico and in the lab), the effect of which has not been adequately monitored. Standard methods recommend analysing silver as soon as possible, due to its inherent instability (APHA 2012).

Table 6.2. Comparison of silver methodologies (units in ppb)

Sample No.	Ag Hach	ICP-MS Filtered	ICP-MS Unfiltered
1	500	321	403
2	490	333	402
3	30	24.1	NA

Notes: ICP-MS values reported as Ag-107 (ppb).
Samples were prepared using silver standards, with a 1:10 dilutions in MQ where required

6.3.2 LIMITATIONS OF FIELDWORK

The planning of fieldwork involving water quality sampling in remote areas is a complex affair. An apparently trivial matter, for instance, affected the collection of a more complete set of data during the first round. For the ICP/IC samples to be shipped back to the UK, a number of small 30 ml plastic bottles were provided in London before departing. These bottles are usually made from LDPE, containing a certified low trace of metals, and were much harder to come by in Mexico than was previously thought before departing. Furthermore, due to commitments with the Municipal authorities, in exchange for their support and financing of some of the local lab testing, samples from major wells in the region had to be collected and analysed in London, as discussed in the methodology (3.2.4). Thus, there were simply not enough bottles to collect all the anion and cation samples desired in the RWH systems, and a selection had to be made. There are no lab suppliers to speak of in San Miguel so purchases had to be done in Mexico City (4 hours by bus) or elsewhere, with deliveries being inordinately slow in many cases.

This, coupled with delays incurred with the logistical setup of the project, as well as difficulties in procuring transport, made the final result quite different from the original plan. Duplicates could also not be taken, which would have made for a much more robust data set.

Many of these hurdles were resolved in the second sampling round, given the past experience (for example, a larger number of sampling bottles were provided from the start). Contacts and arrangements had already been set up before, and there was the necessary know-how to better understand what was required before parting to the sites. Planning was also more realistic. There was the disadvantage of not being able to take samples personally on this occasion but relying on a volunteer, while supervising at a distance. However, all sampling visits were carefully documented and recorded, minimising any possible errors related to this. The volunteer from EWB-UK also received training at UCL before leaving to ensure a high level of rigor and quality in sampling technique.

Finally, the weather was more lenient in 2012, even though sampling was done in the actual rainy season. The heavy off-season storms of February 2010 (see 3.2.1), which caused considerable delays to the entire project, were higher in intensity than any of the average months of the rainy season.

Access to the actual sampling points was challenging at times, for instance, if the person in charge of the keys to the pump and filtering boxes was unavailable, or the school was closed for the day. Rural schools in the region have a general tendency to be slightly unpredictable as to closing times, days off, etc. Sometimes this was related to strikes, lack of attendance on behalf of the teachers, or delays owing to difficulty of access (for instance, with heavy rains or roadblocks). It was also not always possible to phone in advance, as many of the schools don’t have landlines and cell phone access is limited in certain zones.

6.4 MONITORING AND MAINTENANCE OF SYSTEMS IN THE FIELD[33]

It must be kept in mind that projects such as these are interventions in their own right. In other words, they will have an impact, however minor, on the structure and social dynamic of a community. With the exception of conventional water supply systems where 100% of the maintenance expense and responsibility will be borne by the Government or some other external agency, which is certainly not the case here, communal leaders, volunteers and residents alike will have to change their organizational structure to adapt to the new infrastructure, with its associated operation and maintenance demands. Since drinking water is such a delicate, vital issue, a great deal of emotional and even political charge can be expected when planning such a project. The very success of the systems, in the long term, will rely heavily on the politics and involvement of these local actors and stakeholders (Chauhan & Bihua 1983).

In this context, it is important to understand why many RWH systems are installed yet fail to operate adequately in the long run, particularly where technical elements such as filters and pumps are involved, or some form of regular maintenance is required. The methodology section (3.2.1) points out to the fact that not all systems originally installed were available in both sampling periods (Table 3.1), partly due to maintenance issues.

The responsibility for maintenance of the systems fell entirely on the community. A small financial incentive was offered by the municipality but did not receive the adequate follow-up and failed to materialise. Intermittent maintenance and supervision has been performed by the contractors along with a local NGO (IRRI-Mexico), on a largely *pro-bono* basis. At the time of writing, most of the systems were in operation, despite these issues.

6.4.1 REASONS FOR FAILURES

The main reasons for a system failing to operate correctly can be loosely divided between those related to maintenance (or the lack thereof), and those linked to the actual system design, as shown in the next section. This can be stated as social vs. strictly technical aspects. In reality, however, most issues probably fall somewhere in

[33] Parts of this section will be included in a peer-reviewed book chapter (Adler & Campos 2014)

between. A vigilant community, actively engaged in the project, will be more likely to prevent or at least spot and report potential problems before they get worse. On the other hand, even the most proactive stakeholders can do little about a pump failing for purely technical reasons or a lack of electricity, for instance, particularly if they don't have the mechanical parts or the know-how to repair it.

Notwithstanding, technical failures that cannot be readily repaired can easily create frustration and eventual apathy towards the system, as was observed in some of the sites. If people don't feel that they can be a part of the solution to a problem, they start losing interest and simply leaving it in the hands of others, creating in turn a larger probability of future failures, resulting in a 'vicious cycle'. The example described above clearly demonstrates this; without external intervention of some sort (from the authorities or contractors, for instance), it is likely that the system would have been eventually abandoned.

This delicate balance between an intelligent, fail-proof RWH design and active social engagement is not always easy to achieve, particularly in remote communities where regular inspection visits are not feasible and much is left to the community itself (White 2009). Despite the fact that all the beneficiaries were left with telephone numbers and contact information should anything go wrong, and in this regard the local authority was quite helpful, providing a bridge between the contractors and the schools or clinics, very few calls were ever received, even when repairs were badly needed. A general tendency was observed, throughout all the sites, to not report problems but rather wait until someone came round for a visit or inspection. Complaints and concerns were thus issued in person, informally, very rarely by phone, and never in writing or by email. It is difficult to assess how much of this is part of the local culture, a wider phenomenon of rural Mexico, or solely the authors' direct experience. More research would be needed in this regard.

The list below details some of the major causes for systems failing, grouped according to the most likely causal factors: design-related, external and/or linked to maintenance. Some of these could arguably fall into more than one category, such as a broken lid which happened for external reasons (i.e. storms), but was not fixed due to a lack of maintenance and/or community participation, which in turn caused water pollution. The detailed analysis of these issues can thus become quite complicated.

Design-related/project delivery failures (faulty components, installation issues, etc.)

- Leaks in cistern, structural problems
- Collapsing or broken lids
- Damaged gutters or downspouts
- Broken pipes or valves
- Pumps or equipment linked to warranty

External factors (i.e. unrelated to maintenance or to project design)

- Safety issues, vandalism, etc.
- Failure in electric supply (which could damage pumps or electric equipment)
- Strong winds or storms (causing overflows or tearing apart of membranes)

Related to community (i.e. maintenance)

- Clogged filters or issues with purification system
- Damaged drinking water spouts
- Poor water quality in cistern
- Lack of cleaning and emptying settling tanks
- Dirty, contaminated rooftops (causing clogging of gutters or pipes)

Theft was not seen to be a significant problem in any of the sites, though some vandalism was reported on rare occasions, mainly affecting the cistern structure or water quality (i.e. hurling of rocks or debris towards cisterns).

As all systems were tested and delivered in fully functional conditions, it is assumed that there were no major preliminary flaws during installation (for example, in the filters, electric wiring or purification units) and that any issues observed later on were either due to a lack of maintenance, or eventual failing of equipment due to external reasons. Most equipment as well as the installation itself, was covered by warranty for the first year, in which inspections were frequent and many minor problems were fixed.

6.4.2 EXAMPLE OF A NON-OPERATIONAL SITE

Although most systems complied with the basic disinfection requisite, slight nuances were observed. Most notoriously, in 2010, one of the systems failed completely to perform (Site #9 in Table 3.1). Despite all the filtering and disinfection mechanisms, there were inordinately high coliform counts at the effluent, making the system temporarily unfit for consumption. Upon closer inspection of the installation, it was noted that the lid of the cistern (made of geomembrane) had collapsed and was partially torn . The water, exposed to the elements, was gradually contaminated with falling leaves and organic debris, becoming turbid and brownish. The settling tank was also heavily contaminated, having not been cleaned in several months. Upon flushing the foul water, an unpleasant smell came out, showing the degree of pollution that had accumulated over time, and further contaminating incoming rainwater into the cistern. The role of the settling tank, which is normally meant to protect the cistern from the largest concentrations of pollutants, was reversed, becoming a focal point for recontamination.

After discussions with the community and several school parents, it emerged that the head teacher had been replaced recently, and the new one was unaware of the

operation of the system. The training provided to the community the previous year was largely lost, even though some parents (mainly mothers) knew about it and had attended the training. Without clear guidance, the system was simply left to perform by itself with little or no maintenance.

The situation was resolved after much intervention and encouraging active participation from school parents and teachers. A new, albeit more informal, training was delivered, reviewing the main maintenance principles, as well as establishing an agenda for specific tasks. Within a few weeks the lid was repaired, a 'cleaning day' was dutifully scheduled, where several parents and staff attended to clear the roof from debris, prune the trees, etc., and the system was back on line. In the 2012 water quality evaluation the system performed impeccably, with zero coliform counts at the drinking taps, and overall good transparency and cistern water quality (Table 4.6).

6.4.3 ABANDONED SYSTEMS

Two of the systems deserve special mention as they were altogether abandoned, and thus not used for the water quality studies. The reasons are highly complex and briefly discussed below, as there are valuable lessons to be learned in each case.

6.4.3.1 Santuario de Atotonilco

Installed at the community's main primary school (Site No. 12 on Table 3.1), this system was controversial from the start. The Municipality wanted one of the RWH systems installed here, as *Atotonilco* is an emblematic site; its Spanish colonial monastery attracts visitors from all over the globe and was named world heritage site in 2008 by the UNESCO, along with the main town of San Miguel de Allende. Furthermore, the community's water wells have a particularly high fluoride concentration (ESF 2006), one of the main motivators for installing the systems in the first place.

However, the school's staff and parents seemed to be less motivated here than those in other communities. One of the reasons cited by the head teacher was the sheer number of students (close to 100), and the lack of sufficient staff to keep an eye out for vandalism, which in her opinion could occur with an above-ground cistern. Due to insufficient funding, it was not possible to offer the option of a buried cistern. Local politics being a strong factor in this particular community, the fact that Augustin Gonzalez (Sites 7 and 8, Table 3.1) had large underground cisterns, even though these systems had been installed two years earlier with different resources altogether, created a potential source of friction and envy. This fact was also casually mentioned by a few other communities, which saw as 'unfair' that one community should get more attention than the other.

The roof in the school chosen for rainwater harvesting belonged to a small classroom in very poor conditions, badly in need of water-proofing and repair. Some community members related the RWH system to the actual state of the roof, and thought that adding gutters or downpipes would somehow damage or put the structural capacity of

the classroom at risk, which created even further resistance. Other rooftops were not feasible as there was no space nearby to put the elevated cistern, so after much negotiation, the proposed site was agreed upon and construction initiated. From the very beginning, community involvement was minimal and the project as a whole was received with much scepticism. This compares sharply with other sites, such as Rancho Nuevo, San Antonio de la Joya or San Miguel Viejo (Table 3.1), where parents, teachers and students helped out with installations from the first days, to the extent of providing food on a voluntary basis to workers and project managers. In essence, the system was not perceived as meeting any specific need or request of the community. It is a common fact in rural Mexico that communities are somewhat cynical and averse to ideas coming from the Government (or perceived as such). This is due mainly to a large history of neglect and complex relationships between the Federal or Municipal authorities and local community leaders. Had the installation offered to refurbish the actual classroom building (an issue which seemed to concern the parents and teachers more), along with the RWH system, it is possible that it would have had a greater receptivity. The Municipal Government, however, was unable to provide this at the time from the allocated funding.

Once the system was installed and tested, it worked well for a short while before it was neglected. On a subsequent visit, the head teacher reported that '*children did not like the taste of the water*'. The lid of the cistern also collapsed due to vandalism (according to the same source), by children climbing onto its side. One of the drinking fountains was broken from a football and never replaced. Despite efforts to keep the system running, including replacing the geomembrane cistern for a hard plastic tank, it was eventually abandoned (Figure 6.4).

Figure 6.4. Abandoned system at Santuario Atotonilco

6.4.3.2 Cruz del Palmar

Cruz del Palmar is the largest community in the Municipality of San Miguel, with over 1000 inhabitants (INEGI 2011). It was established in 1516, and is also one of the geographically farthest from the main town. Until recently, like many of the other sites, it was accessible only via dirt roads, which became difficult to pass during the rainy season. However, a new highway has greatly facilitated connections and transport. The Municipality was keen on installing a RWH system due to poor groundwater quality (same criteria as for other sites), occasional water scarcity and the higher social impact expected from a larger population.

The choice of the site was agreed with the *Delegado*, a local political figure in Mexico which stands for a community representative of sorts, and the main link in the hierarchy with the Municipal authorities. He (or she) is usually elected every 3 years. Dealing with an elected representative, in contrast with a long-term and well established head teacher or community leader, presents important challenges. The short period means that any commitments and follow-up to projects might not necessarily be honoured by the successor. This can also depend highly on kinship and political affiliations. The level of interest a project may receive could be well dependent on how much longer is the term, how seriously committed is the representative to the community at large, or even the political advantage, if any, that can be gained from the project. The same reasoning applies to Municipal and Federal programmes, though in the latter case governing periods are usually longer (up to 6 years). Such variation in the water management agenda due to the frequent political succession is commonplace in Mexico (Adler 2011).

The site selected was a large communal space, known as a 'Multiple-use Hall', where weddings, meetings and local celebrations take place. The key to this space is usually in the hands of the *Delegado*, and it locked while not in use, as no staff reside or operate within it on a regular basis. The plan was to install the cistern *inside* the Hall, fencing out an internal area for the purpose, and channel rainwater from its large metallic roof into it. The water, after purification, would be sent across a small street to the local clinic, where two drinking taps were installed for public use. This technically challenging and expensive project was completed and delivered, along with a training session to the clinic staff and local authority, as scheduled. The session, however, in contrast to other communities, had very low attendance. It was also difficult to know who was going to be in charge of the system, as the clinic staff had a high rotation, and the Delegate was about to complete his 3-year term. After a while of having installed the system, the community protested that it was taking up too much space of the Hall, and that it would be best to remove it.

The new representative seemed receptive and keen restart the system, arranging a meeting with the town residents and putting it at the top of his agenda. After several visits, it was agreed to physically move the system to the local secondary school (the community is large enough to have one, most of the others only have primary schools). The head teacher there was highly interested, along with several of the parents, and the entire system, including the 30,000 litre geomembrane cistern (which

being portable, was loaded onto a large truck), all the gutters, pipes and filters, was installed in the new location.

6.4.4 IMPACT OF COMMUNITY PARTICIPATION AND LEADERSHIP

Table 6.3 attempts to correlate overall performance of the system with the degree of involvement (Participation column) and leadership present during the evaluation period, whether by official figures (such as head teachers) or informal community leaders, who decided to 'champion' the project. In general terms, participation does not refer so much to actual installation, but to the on-going maintenance and involvement of the community with the system. In order to assess efficiency water quality indicators were used, mainly COD and coliform bacteria, comparing the reduction in these variables from the entry point (settling tank) to the drinking water tap (see 6.1). 'Overall condition' refers to the observed state of the system, including aspects such as cleanliness, leaks, condition of pipes and cistern lids, and other general maintenance issues.

In order to have a standard basis for comparison, the following (somewhat subjective) scale was utilised for all the parameters listed in Table 6.3:

+++ Excellent

++ Satisfactory

+ Average

- Missing or lacking altogether (i.e. very poor conditions)

In the 'Leadership' column, a negative score (-) refers to a complete lack of clear leadership, and a '+' (average score) to communities that had a high rotation of head teachers, for instance, even though they may have been highly involved with the project at some particular period. In these cases, there may not have been an adequate transfer of skills and responsibilities.

Table 6.3. Comparative of system performance and community participation*

ID	Community	Overall condition	Efficiency	Participation	Leadership
1	Rancho Nuevo V. Guadalupe	++	+++	+++	++
2	San Antonio de la Joya	+	++	++	++
3	Don Juan	++	+++	++	+
4	La Aurora	++	-	+	-
5	San Miguel Viejo – Classroom	+++	++	+++	+++
6	San Miguel Viejo – Kitchen	+++	+++	+++	+++
7	Augustin Gonzalez – Clinic	+	+	+	-
8	Augustin Gonzalez – School	+	+++	++	+
9	El Salitre	+	++	++	+
10	Montecillo de Nieto	+	+++	+	+++
11	Boca de la Cañada	++	++	++	++

* Based on most recent data available for each site

It can be observed from Table 6.3 that communities with greater participation and leadership tended to fare better in terms of water quality and system performance. However, strong leadership in and of itself did not necessarily guarantee satisfactory results (Site No. 10). There were also instances where there was a strong community involvement without clear leadership (Nos. 8 and 9), but even if efficiency was high, the overall condition and maintenance of the system tended to suffer as a consequence.

The issue of high rotation of local leaders (whether they be head teachers or elected representatives) is hard to resolve, particularly in schools and clinics. This can be partially circumvented by identifying early on influential people in the community who are not necessarily linked to the more transient roles of power or authority. This was the case in one such community (Site No. 1), where despite a very high rotation of the local school's head teachers, the system fared with excellent outcomes (in Table 6.3) thanks to the participation of local residents and parents, who were perceived as proactive 'leaders' by the community, even if they didn't have any formal role. The high level of organisation and involvement of such individuals from the start has guaranteed the continued success of the programme on this particular site.

6.4.5 *TRAINING AND SUCCESSION*

A phenomenon commonly observed in projects that are 'handed down' to communities by NGOs or public programmes is the lack of follow-up and stakeholder succession, particularly once the project has stepped out of the limelight and any political objectives have been achieved (in the case of Government projects). In the community of Montecillo de Nieto (Site No. 10), for instance, an ambitious dry toilet installation for the entire school had been abandoned for a number of years. Taking up valuable space, and attracting flies and odours for a long period, it created a problem instead of a solution for the beneficiaries. When questioned about it, the head teacher vaguely mentioned a 'foreign NGO' which had donated the project[34], no doubt with the best of intentions, but with no follow-up on behalf of the community or the organisation.

The mechanism in which this can occur was observed repeatedly with the RWH systems of the present study. The budget for all the installations included a training programme and the elaboration of an illustrated manual, so that users could know exactly what maintenance was required, where to purchase the necessary supplies and who to address in case of problems, both with local private contractors and in the Municipal Government (as mentioned before, little use was made of these contacts). These training sessions were all duly completed, with signed commitments to maintain the systems. Some of the most pro-active communities even implemented 'water committees', to follow up and pass the knowledge on to the future generations of parents in the schools, or staff in clinics. Many of the projects at the start received great pomp and attention from the local press. In the more prominent sites, the city Mayor came in person, along with State officers and other leading figures, to attend a formal inauguration ceremony, with lofty speeches and offers to continue expanding the RWH agenda, as well as supporting the communities with some funding for yearly maintenance. There was never any formal commitment on the later, but the very promise of it created a sense of expectation in the inhabitants, purportedly not conducive to encouraging responsibility for the care of the systems.

After one or two academic years had passed, groups of children left primary school and along with them parents who had been involved with the projects from the beginning. On a few occasions staff and head teachers changed too, creating a widening gap which resulted inevitably in poor maintenance and lack of understanding as to the operation of the systems. During the 2012 sampling round, for

[34] Personal communication (June, 2010). Name withheld.

instance, it was noted in some communities that user manuals had been lost, or keys been misplaced, barring access to the filters and pumps. In the case of clinics, this became even more complicated, as doctors and nurses rotate regularly in rural Mexican health centres. Some training sessions were repeated on request for the new generations, on a *pro bono* basis, but without any funding this became increasingly difficult.

6.4.5.1 Technical complexities

Another lesson learned was that of technological know-how, and the form in which this was transmitted to beneficiaries. Although most community members were familiar with the idea of a filter, a basic water pump or a cistern, the silver ion unit was an unknown component that tended to baffle many. For the sake of simplicity, they were instructed, both in training sessions and in the user manuals to inspect the cells only once a year and report any anomaly with the device, such as the indicator lights being off or malfunctioning. Although this was not complicated in and of itself, the fact that not enough effort was put into explaining the mechanism of how it worked, created a certain 'distancing' and apathy, which could be translated as a fear of tampering with the unit. This lack of familiarity resulted in the silver ion units never being inspected or replaced by the community members, even in those sites where other maintenance activities were dutifully carried out, such as emptying setting tanks, cleaning cisterns and roofs, etc. Their approach to these somewhat sophisticated units as a mysterious 'black box', generated issues with their upkeep and the necessity of external technicians to do simple maintenance tasks which could otherwise have been locally dealt with.

In schools, which represent the majority of scenarios studied, children were also not involved enough in general. Rather, it was left to the teachers to decide how best to involve or inform them of the significance of the system. It is the opinion of the authors that more effort in this direction would have greatly enhanced the project's capability and social participation. Not only for the direct educational value of such an endeavour, but also partly for ensuring the continuity of the system itself. In the case of Santuario de Atotonilco, for example (one of the 'abandoned systems' described previously), the incidence of vandalism could have been reduced with greater involvement.

This chapter has attempted to present an overall assessment of the research project, including the comparison between both fieldwork periods, where an improvement in many of the parameters is observed (albeit without sufficient evidence for establishing conclusive trends), and continuing with other issues of key importance, such as applicability of the lab work to the field, research limitations, possible sources of error and social aspects related to maintenance and community participation. The conclusions inferred from these analyses are presented in the next and final chapter of this dissertation.

7 CONCLUDING REMARKS

7.1 CONCLUSIONS

A) Silver ion generation is strongly correlated to conductivity and ionic strength, and in consequence is observed to behave very differently in RW compared to other sources. It is expected that in waters containing more minerals, anions and other substances, the silver ions will complex with other elements or precipitate out of solution faster (Landau 2007). Most silver ion systems are built for use with common water supplies, such as tap water. It is proposed in this project that the case of RWH is unique and deserves special attention, due to its reduced content of precipitating anions (such as chloride) and lower conductivities, with the following observed consequences:

- Silver generation takes place at a slower rate than in tap water or groundwater, due to more conductive water. This does not imply greater power consumption, as the electric current flowing through the ionisation device is correspondingly reduced, according to equation 5.2 (section 5.4). It does affect, however, the ionisation time needed to reach a desired silver concentration.

- Experimental results with RW show that, using the full-cell device, silver concentrations of 300 – 400 ppb can be reached in batch experiments within a few minutes (5.1.2), or around 190 ppb in continuous flow operation (5.2.1.1), with typical flow rates of 1.0 Lpm, at a voltage setting of approximately 5V. Ionisation under similar conditions in tap water will reach significantly higher values, and correspondingly lower in DI.

- This silver concentration attained in RW (190 ppb) under constant flow conditions which are common in the field, is deemed enough to inactivate the bacterial (*E. coli*) and viral (bacteriophages) indicators utilised in the lab (see section 5.3).

- Silver ions diffuse better and faster in lower conductivity waters such as DI, and very little in tap water. RW is somewhere in between, depending on the particular conductivity and ionic strength of the sample. Silver ions are not seen to diffuse backwards under continuous flow operation, nor ‘uphill’ (against gravity), in the concentrations tested here. Exceptions are seen for DI and for RW only under stagnant conditions and for a prolonged period (see sections 5.1.5, 5.2.2.2 and 5.2.3.1).

- Following from the above arguments, silver ions are confirmed to have slower decay rates in RW than in higher conductivity waters (5.1.6).

- In consequence, silver ionising systems applied to RWH have the advantage of longer residual times and longer duration of the silver cells, given the slower consumption rate, while generating sufficient concentrations for effective disinfection.

- The situation is reversed, however, for rainwaters with a high organic matter or nutrient load, as observed from the experiments shown in 5.1.6.3. Judging from water quality values obtained from the field (Ch. 4), it is preferable to position the ioniser after settling and/or some sort of preliminary filtration, where the larger volumes of contaminants from rooftops or from atmospheric deposition will have been removed.

B) Another conclusion reached by this study is that the ionisation devices currently used in the field can be optimised by the following simple and low cost improvements:

- Redesign the *ionisation chamber* or vessel so as to increase retention time (5.5.6.3), placing the cells in a way that will maximise contact time (i.e. parallel to the flow).

- Many systems operate by alternating polarities from one electrode to the other. Despite the benefits in reducing scaling, this was observed to be inefficient and to cause current peaks which diminish silver ion production while wasting energy. Longer switching times are suggested, as discussed in 5.4.5.2.

- A correlation between turbidity and silver generation has been suggested, which could help to rapidly monitor, though with limited accuracy, the adequate functioning of an ionisation device (5.5.4).

C) A proposed contribution of this work is an increased focus on the electrical parameters of the ionisation process. The main lessons learned from this are:

- Electric current seems to consistently increase with water flow in the tests performed, for reasons not fully understood. This implies that correspondingly higher amounts of silver will be released as the water flow rises, which is beneficial to the operation of the system (i.e. since higher flows tend to dilute existing silver concentrations), and should be taken into account when designing for energy optimisation (5.4.3).

- Batch experiments have shown, despite the limited data obtained, a confirmation of the theoretical linear regression model adapted from Faraday's law and Ohm's law. This allows for the eventual construction (with more data) of a valuable empirical model that can be used to predict silver concentrations from parameters that are easily measurable in the field (5.5.6).

D) Community participation and leadership are observed to be closely linked to the level of maintenance performed on the systems. Training and succession are also seen to be important factors to guarantee the overall success of the projects.

7.2 SUGGESTIONS FOR FUTURE WORK

From a purely technical perspective, the following recommendations can be made for future research:

- Obtain more data points in batch experiments, involving the different devices, in order to perfect and refine the linear model suggested in equation 5.9 (section 5.5.6.2).
- If access to an ICP-MS is feasible, it is suggested to perform all samples with this, due to its greater accuracy and the possibility of analysing larger numbers of samples in each run. This should be done after establishing a consistent and functional methodology, using lab spectrophotometry and other colorimetric techniques for confirmation.
- Adding water meters in the field would be helpful, to know the total volume of water that has been processed and correlate this to silver wear on the electrodes, for instance. Rain gages on each site, along with improved weather data, would also be helpful to gain a better understanding of the changing rainwater quality of the systems.
- The turbidity experiments discussed in section 5.5.4 are to be taken as preliminary indicators of a potentially valuable correlation. More studies should be done, including in the field systems, as well as analysis of the sediments generated, to better understand and apply this phenomenon.
- During electrolysis, the 'bubbles' observed on the cathode are presumably hydrogen (Table 5.2). An interesting future research would be to find ways to harness the gas, and possibly accumulate it at low pressure for future use in fuel cells or for direct ICE (Internal Combustion Engine) applications.
- From the experimental data, it seems that excessive silver ion concentrations are being generated with the full-cell device in RW at the flow rates used (5.2). To avoid the phenomenon colloquially known as 'overkill', which is wasteful of valuable resources such as silver and electric energy, it would be recommended to better determine the optimum voltage for the minimum silver concentration required. It is likely that the current setting of 5V is too high for most practical applications (particularly if the device is redesigned and optimised as suggested in the previous section). Reducing the voltage would prevent the electrodes from unnecessary degradation and increase the overall cost-effectiveness of the system.
- The precipitates generated from experiments (particularly in tap and RW) could be analysed using a scanning electron microscope (SEM), using the element analysis function. Preliminary tests were successfully performed with this (not reported here). SEM can also be used to gain a better understanding of the effect of the silver ions in bacteriophages, though the resolution might be insufficient (in which case a Transmission Electron Microscope, if available, could be a better option).

The recommendations listed below, gained from the practical experience of this research study, could be useful for future projects where a high level of community participation is required (as a follow up to the discussion on 6.4):

- Ensure the system meets a genuinely perceived need of the community.
- Identify leadership and follow-up responsibilities from all stakeholders from the start.
- Ensure a robust design, which requires the minimum (or the simplest) maintenance possible.
- Involve beneficiaries (i.e. school children) as much as possible, explaining system operation, etc.
- Ensure that contact details for problems and emergencies are clearly posted in accessible locations.
- Whenever feasible, ensure site visits/ inspections on a regular and predictable basis.
- Ideally, choose technology that is easy to repair and maintain, with consumables that are locally available.

As a final comment on the RWH system *per se*, it was observed that the majority of problems did not occur with the silver ioniser or the filters, but with the settling tanks and cisterns, an issue more related to the overall design, and not particularly covered in this thesis. Notwithstanding, a potential improvement can be made by replacing the settling tank for a modern first-flush device, as amply suggested in the literature (Abbott et al. 2007; Ward et al. 2010). The first flush mechanism can be enhanced to allow for a better drainage or 'self-cleaning', avoiding stagnating water which increases the risk of contamination, while easing the maintenance burden for the community. The importance of proper innovation and design in this regard cannot be overlooked.

In summary, it can be stated that the systems in the field, with all their components (settling tank, filters and silver ioniser) have the potential to provide quality drinking water from harvested rain as long as reasonable and routine maintenance is performed (i.e. flushing of settling tanks, roof cleaning, etc.). It is the hope of the author that the findings from this doctoral research will contribute to the improvement and better understanding of such systems, and to the improvement of overall quality of life in rural communities.

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ANNEXES

A) DATA TABLES

SPSS VARIABLES: GENERAL DATA

Name	Type	Decimals	Description
Date	Date	0	Month/year of Experiment
ExpLabel	String	0	Experimental label/reference
Model	Numeric	0	Lab model [Cont/Batch]
Device	Numeric	0	Device Type
Water	Numeric	0	Water source
Powersupply	Numeric	0	Power supply
Sample_label	String	0	Sample label (optional)
Sample_run	Numeric	0	Sampling round number (in same exp)
Sample_Pt	Numeric	0	Sampling point
Voltage	Numeric	2	Voltage
Volume	Numeric	1	Volume in ml
Container	Numeric	0	Container type
Flow	Numeric	1	Flow in Lpm
CANG	Numeric	0	Cell Angle to flow
Ag_ICP	Numeric	1	ICP-MS (ppb)
Ag_Hach	Numeric	1	Hach (ppb)
Ag_actual	Numeric	1	Ag used as final data value (Hach or ICP)
Time_ion	Numeric	1	Time with ioniser ON (all decimal)
Time_out	Numeric	1	Mins. AFTER turning OFF (cell contact)
Time_flow	Numeric	1	Mins. pump ON/Flow during Exp.
Cond	Numeric	1	Initial conductivity (µS/cm)
Cond_now	Numeric	1	Conductivity (µS/cm)
pH	Numeric	2	pH
TDS	Numeric	2	Total Dissolved Solids (mg/l)
Temp	Numeric	1	Temperature (C)
TOC	Numeric	2	TOC (mg/l)
Turb	Numeric	2	Turbidity (NTU)
Colour	Numeric	0	Visual colour obs.
Notes	String	0	General Observations
Time_pre	Numeric	1	Mins. BEFORE ioniser ON (in contact)

SPECIFIC VARIABLES FOR ELECTRIC CURRENT MEASUREMENTS

Ipeak	Numeric	2	Peak current mA
Istable_time	Numeric	0	Time (secs) for current to stabilise
I	Numeric	2	Current (mA)
Dist	Numeric	1	Dist between electrodes/wire (cm)
HSUB	Numeric	0	Height submersed Electrode/wire
SUBVOL	Numeric	2	Total volume submersed (cm3)
AREA	Numeric	1	Electrode Area (cm 2)
Wire_diam	Numeric	1	Average diameter of wire (mm)

Batch tests

Water	Powersupply	Voltage	Volume	Ag_ICP	Ag_Hach	Time_ion	Cond	pH
DI	SilverLife	12.74	900	NA	620	25.0	110.0	6.5
DI	SilverLife	9.97	300	27.30	NA	5.0	2.0	NA
DI	SilverLife	9.97	300	44.20	NA	11.0	2.0	NA
DI	SilverLife	9.97	300	24.40	NA	11.0	2.0	NA
DI	SilverLife	9.97	300	24.10	NA	11.0	2.0	NA
DI	Fixed	5.03	400	NA	NA	0.1	2.0	6.1
DI	Fixed	5.03	400	NA	NA	0.1	2.0	6.1
DI	Fixed	5.03	350	NA	410	10.2	2.0	6.2
DI	Fixed	5.06	400	NA	0	0.0	2.0	5.6
DI	Fixed	5.05	400	NA	140	5.0	2.0	5.6
RW	SilverLife	0.00	300	0.40	NA	0.0	52.5	6.4
RW	SilverLife	9.97	300	NA	460	11.0	52.5	NA
RW	SilverLife	5.08	10000	21.00	30	5.0	125.0	7.0
RW	SilverLife	5.08	10000	75.72	NA	10.0	125.0	7.0
RW	SilverLife	0.00	900	NA	0	0.0	82.0	6.8
RW	SilverLife	5.00	900	NA	630	10.0	82.0	NA
RW	Fixed	10.18	750	NA	0	0.0	170.0	7.6
RW	Fixed	10.18	750	NA	670	17.5	170.0	8.2
RW	Fixed	5.04	400	NA	0	0.0	120.0	NA
RW	Fixed	5.02	350	NA	830	10.2	120.0	NA
RW	Arduino	4.85	220	NA	NA	3.5	112.5	NA
RW	Arduino	0.00	200	NA	0	0.0	NA	NA
RW	Arduino	4.97	200	NA	1040	24.0	NA	NA
TAP	SilverLife	5.00	10000	NA	705	10.0	770.0	NA
TAP	Fixed	10.00	700	NA	910	22.0	531.0	NA
TAP	Fixed	10.00	500	NA	0	0.0	670.0	8.1
TAP	Fixed	10.00	500	NA	940	7.0	670.0	8.6
TAP	Fixed	9.50	800	NA	NA	5.0	635.0	7.9
TAP	Battery	9.50	800	NA	NA	1.0	635.0	7.9
TAP	Fixed	5.00	800	NA	NA	1.0	635.0	7.9
TAP	Fixed	5.10	250	NA	NA	0.1	658.0	NA
TAP	Fixed	9.54	250	NA	NA	0.1	658.0	NA
TAP	Arduino	4.97	220	NA	NA	1.0	650.0	NA

Note: Tests shown for half-cell device only

Continuous flow (Model I)

Powersupply	Pt	Voltage	Flow	CANG	Ag_Hach	Time_ion	Cond	pH
SilverLife	1	5.05	0.5	NA	0	1.0	NA	NA
SilverLife	3	5.05	0.5	NA	390	1.0	NA	7.0
SilverLife	2	0.00	0.0	NA	10	1.0	NA	NA
SilverLife	2	5.06	0.9	NA	180	30.0	138.0	NA
SilverLife	2	5.01	1.0	NA	0	1.0	NA	NA
SilverLife	3	5.01	1.0	NA	190	1.0	NA	NA
SilverLife	3	5.00	0.5	NA	190	5.0	NA	NA
SilverLife	3	0.00	0.0	NA	20	5.0	NA	NA
SilverLife	3	5.00	0.8	NA	40	1.5	NA	NA
SilverLife	3	5.00	0.8	NA	460	3.0	NA	NA
SilverLife	3	5.00	0.8	NA	760	6.5	NA	NA
Fixed	3	5.08	0.6	0	330	1.0	82.4	7.0
Fixed	3	0.00	0.0	0	60	1.0	82.4	6.9
Fixed	2	5.04	0.6	0	NA	1.0	NA	NA
Fixed	3	5.04	0.6	0	NA	1.0	NA	NA
Fixed	1	5.02	0.6	NA	NA	0.0	70.4	7.0
Fixed	3	5.02	0.6	NA	400	2.4	72.7	6.9
Fixed	3	5.02	0.6	NA	NA	2.4	72.7	NA
Fixed	4	5.02	0.6	NA	10	2.4	101.4	7.4
Arduino	3	4.79	1.0	0	0	0.0	73.9	6.8
Arduino	3	4.79	1.0	0	90	1.0	73.9	6.9
Arduino	3	4.79	1.0	0	60	4.0	73.9	6.7
Arduino	3	4.79	1.0	0	70	8.0	73.9	6.8
Arduino	4	4.79	1.0	0	0	1.0	66.6	6.9
Arduino	4	4.79	1.0	0	10	4.0	66.6	6.6
Fixed	3	4.80	0.0	90	NA	1.0	70.0	NA
Fixed	3	4.80	1.0	90	NA	1.0	70.0	NA
Fixed	3	4.80	1.0	90	NA	2.0	70.0	NA
Fixed	3	4.80	1.0	90	NA	2.0	70.0	NA
Fixed	3	4.80	0.3	90	NA	1.0	70.0	NA
Fixed	3	4.80	1.5	90	NA	1.0	70.0	NA
Fixed	3	4.80	1.4	0	NA	1.0	70.0	NA
Fixed	3	4.79	1.0	0	NA	0.0	70.0	6.6
Fixed	3	4.79	1.0	0	160	1.0	70.0	6.6
Fixed	3	4.79	1.0	0	190	4.0	70.0	6.7
Fixed	3	4.79	1.0	0	190	8.0	70.0	6.4
Fixed	3	4.79	1.0	0	NA	0.0	76.2	6.7
Fixed	4	4.79	1.0	0	0	1.0	76.2	6.8
Fixed	4	4.79	1.0	0	NA	4.0	76.2	6.7
Fixed	4	4.79	1.0	0	60	8.0	76.2	6.9
Fixed	4	4.89	1.0	0	NA	4.0	68.6	7.1
Fixed	3	0.00	1.0	0	70	8.0	70.0	6.8
Fixed	3	4.87	1.0	90	200	4.0	90.0	NA
Fixed	4	4.87	1.0	90	40	4.0	90.0	NA

Note: Sampling points refer to Figure 3.13.
All runs are in RW for this model

Date	Conductivity (µS/cm)	pH	Source	Instrument
15/11/2011	0.8	NA	DI	Jenway
19/01/2012	1.5	6.1	DI	Jenway
30/01/2012	1.6	NA	DI	Jenway
25/09/2012	5.5	5.22	DI	Mettler-Toledo
27/09/2012	5.9	5.5	DI	Jenway
05/10/2012	4.41	5.52	DI	Mettler-Toledo
08/10/2012	1.91	6.25	DI	Mettler-Toledo
MEAN	**3.1**	**5.72**		
28/09/2011	50	6.7	RW	ECTestr
14/11/2011	52.5	6.4	RW	Jenway
30/01/2012	95	7.1	RW	Jenway
06/03/2012	90	7.0	RW	Jenway
25/10/2012	59	6.5	RW	Jenway
13/11/2012	60	NA	RW	Jenway
22/11/2012	70.4	7.0	RW	Mettler-Toledo
MEAN	**68.1**	**6.85**		
03/06/2011	650	NA	Tap	ECTestr
16/02/2012	770	NA	Tap	ECTestr
06/03/2012	800	NA	Tap	ECTestr
25/09/2012	635	7.9	Tap	Mettler-Toledo
27/09/2012	692	8.1	Tap	Jenway
04/10/2012	657	NA	Tap	Mettler-Toledo
13/11/2012	650	NA	Tap	Jenway
24/09/2012	688	8.1	Tap	Mettler-Toledo
MEAN	**692.8**	**8.03**		

B) SAMPLING METHODOLOGY IN THE FIELD

Procedure:

The following standard methodology was approved for use in collecting field samples, to ensure a high standard of data consistency. It was rigorously implemented in both rounds.

1. Take 2 water sub-samples in clean 30 ml plastic containers, fill to the top and make sure that the water comes over the top of the bottle in a dome. Cap the bottles immediately after taking the sample and place in cooler. These samples will be transported to UK, and identified as:

a. Anions

b. Cations, for these add 1-2 drops of HNO3, or until pH is about 2 or less

2. Take one extra sample, with the same procedure (without adding HNO3), for analysis in the local lab, as well as microbiology samples in the appropriate bags.

3. Ideally take water samples before chlorination or treatment (directly from wells, or from rainwater cisterns). When taking samples from wells, purge at least one well volume before sampling (to remove stagnant water). For rainwater samples and drinking taps, allow to flush for a few seconds before sampling.

4. Take and record other readings such as Temperature, pH, conductivity and DO for each sample.

Labelling:

All labels will contain the following numerical code:

Site No. (1-6)	Sub-site (a,b,c,d,e)	Sample number	Sample type (P, M, etc.)	Lab (E for England or L for 'Local')	Sub-sample: anions (-) or cations (+)

Site & sub-sites

Site number refers to the community or system being sampled; sub-site refers to the actual sampling point (b: settling tank, c: cistern, etc.). This varied slightly between the 2010 and 2012 round, as an extra point was added in the latter (see Table. 3.4).

Sample Number

This will contain 3 digits and registered consecutively, starting from 001, regardless of the dates when the samples are taken (which is registered separately).

Sample Type

Depending on what will be analysed, these will carry the corresponding letter:

P – Basic or General Parameters (mostly chemistry), including Silver.

M – Microbiology, in this case the container will be of 100 ml.

N – Nutrients (if a separate sample is required for this), etc.

Lab

Indicates whether sample is meant for transport to England (E) or Local lab (L).
The following information shall also be recorded on the label:

- Date and Time of sampling
- Name of community or place
- If the sample is a DUPLICATE or a BLANK, this must be clearly indicated

C) PUBLICATIONS

The following publications related to this research were done as follows (not included in the electronic version of the thesis for copyright reasons):

Conference papers

- Adler, I. et al., 2012. Evaluation of a silver ion system for rainwater purification using bacteriophage indicators. In *3rd IWA - RWHM Conference, 20-24 May*. Goseong, Korea: IWA.

Papers in peer-reviewed journals

- Adler, I., Hudson-Edwards, K.A. & Campos, L.C., 2011. Converting rain into drinking water: quality issues and technological advances. *Water Science & Technology: Water Supply*, 11(6), p.659-667

- Adler, I., Hudson-Edwards, K.A. & Campos, L.C., 2013. Evaluation of a silver-ion based purification system for rainwater harvesting at a small-scale community level. *Journal of Water Supply: Research and Technology—AQUA*, 62(8), pp. 545-551

Book Chapters

Adler, I., Campos, L.C. & Bell, S., 2014. Community participation in decentralised rainwater systems: a Mexican case study. In A. M. Fayyaz & S. Ward, eds. Alternative Water Supply Systems. Exeter: International Water Association (IWA).

Tahir, S., Adler, I. & Campos, L.C., 2014. Rainwater Recycling in Buildings. In K. Adeyeye, ed. *Water Efficiency in Buildings: theory and practice*. Oxford: John Wiley & Sons, pp. 190–206.